

Section 4

ANTIMONY

US EPA RECORDS CENTER REGION 5



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Antimony (Sb) is a multivalent element with Sb(III) species $[Sb(OH)_3^0]$ dominant under reducing conditions and Sb(V) species $[Sb(OH)_6^-]$ dominant under oxidizing conditions. Antimony (V) forms several polynuclear species in aqueous solutions; these species contribute significantly to the total Sb only at high Sb concentrations ($>10^{-2}M$). All of the known Sb compounds are very soluble; therefore, Sb concentrations are not expected to be solubility limited. Very little is known about adsorption/desorption behavior of Sb. Because of its anionic character under oxidizing conditions, adsorption by hydrous oxides at low pH values may be significant.

RELATIVE STABILITY OF SOLID AND AQUEOUS SPECIES

Antimony^{is} a multivalent element^{that} exhibits -3, 0, +3, and +5 valence states. Antimony (III) and (V) are the stable oxidation states in aqueous solutions. Most of the Sb(V) compounds are very soluble and Sb in nature primarily occurs as Sb_2S_3 or Sb_2O_3 (Baes and Mesmer 1976). Thermodynamic data (see Appendix A, Table A-1) were used to predict the geochemical behavior of Sb. Figure 4-1 illustrates the dominant aqueous species for the Sb-H₂O system. The Sb(V) species $[Sb(OH)_6^-]$ is predominant in oxidizing environments ($pe + pH \geq 11.4$) and at pH values >2.8 . The Sb(III) species $[Sb(OH)_3^0]$ is predominant in relatively reducing environments ($pe + pH \leq 11.4$) at pH values between 1.5 and 11.2.

The distribution of Sb aqueous species in equilibrium with Sb_2O_3 (cubic) is illustrated in Figure 4-2. As expected, $Sb(OH)_3^0$ is the predominant hydrolysis species at low redox potentials with $Sb(OH)_6^-$ becoming increasingly important at high redox potentials. The species $Sb_2S_4^{2-}$ will be important in reducing environments if the total sulfide concentration exceeds $10^{-6.0} M$. Figure 4-2 also shows that the concentration of Sb in equilibrium with Sb_2O_3 will be a function of pH and Eh and will always be equal to or greater than $10^{-4.2} M$.

Figures 4-3 and 4-4 show the distribution of Sb(V) species as a function of pH. The only known Sb(V) solid phase, $Sb_2O_5(c)$, is highly soluble. Therefore, various total concentrations of Sb were examined. At $0.001 M$ total Sb, $Sb(OH)_3^0$ and $Sb(OH)_6^-$ are

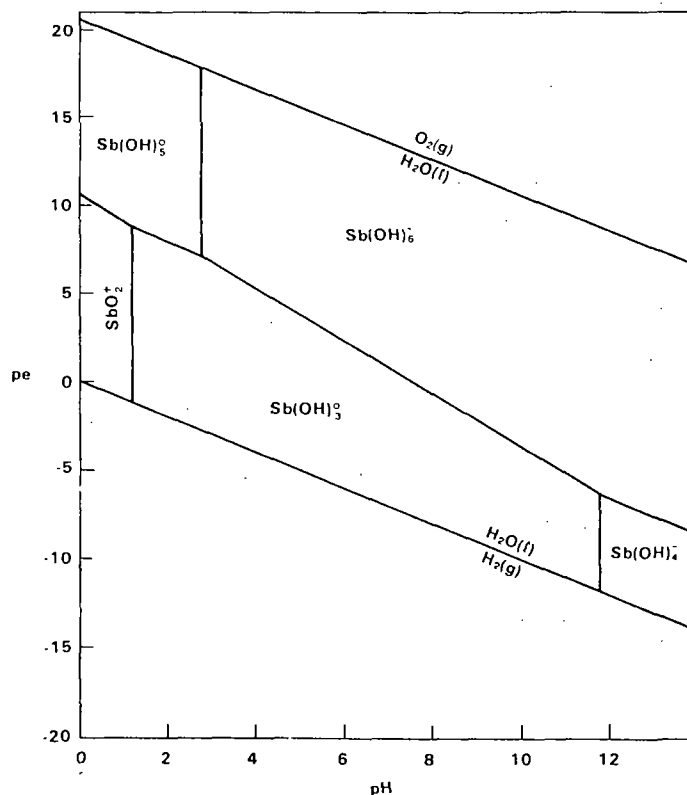


Figure 4-1. pe-pH diagram for Sb-H₂O system, at 25°C. The outlined regions indicate the conditions under which the given Sb solution species is predominant.

the dominant species with the polynuclear species $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ and $\text{Sb}_{12}(\text{OH})_{65}^{5-}$ present in very small quantities. The Sb(III) species [$\text{Sb}(\text{OH})_3^0$, $\text{Sb}_2\text{S}_4^{2-}$, $\text{Sb}(\text{OH})_4^-$] will be unimportant except in reducing environments. As with all polynuclear complexes, the importance of the $\text{Sb}_{12}(\text{OH})_x$ species increases as the total Sb increases. In Figure 4-4, the $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ species is dominant near pH 2 when total Sb is 0.01 M. It should be noted that at low pH, even though the concentration of $\text{Sb}(\text{OH})_5^0$ is slightly higher than $\text{Sb}_{12}(\text{OH})_{64}^{4-}$, the $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ actually contains a far greater fraction of the total antimony because of the 12 Sb atoms per molecule of polynuclear complex.

Even though fairly high Sb concentrations were selected for Figures 4-3 and 4-4, the solubility products of known Sb solids are never exceeded. The Sb species under oxidizing environments and the environmental range of pH are negatively charged; therefore, one would expect Sb to be highly mobile in oxidized environments. The solubility of Sb as a function of redox is further illustrated in Figure 4-5 in

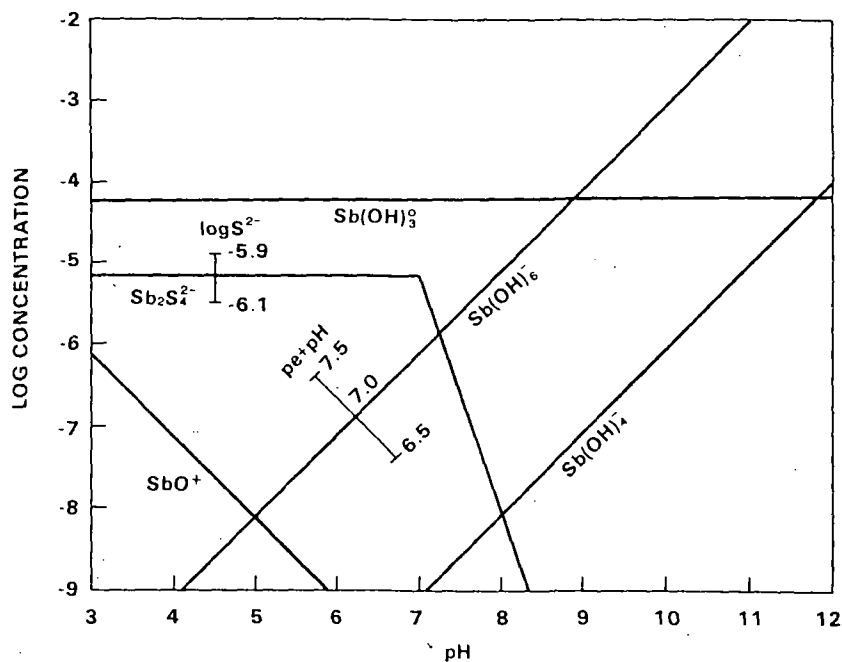


Figure 4-2. The activities of Sb(III) aqueous species along with a Sb(V) species [$\text{Sb}(\text{OH})_6^{3-}$] in equilibrium with $\text{Sb}_2\text{O}_3(\text{c})$.

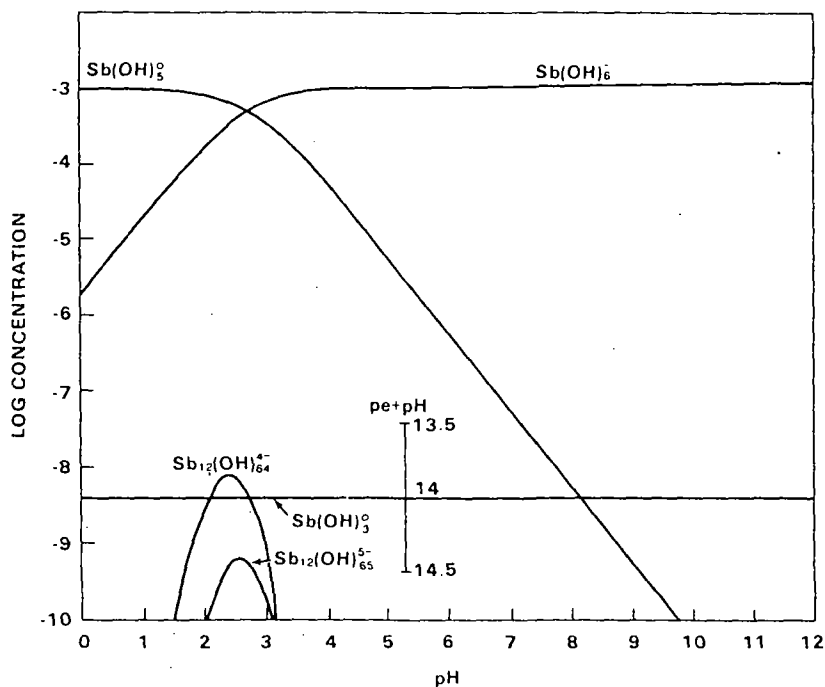


Figure 4-3. The equilibrium concentration of Sb(V) species in 0.001 M total Sb(V).

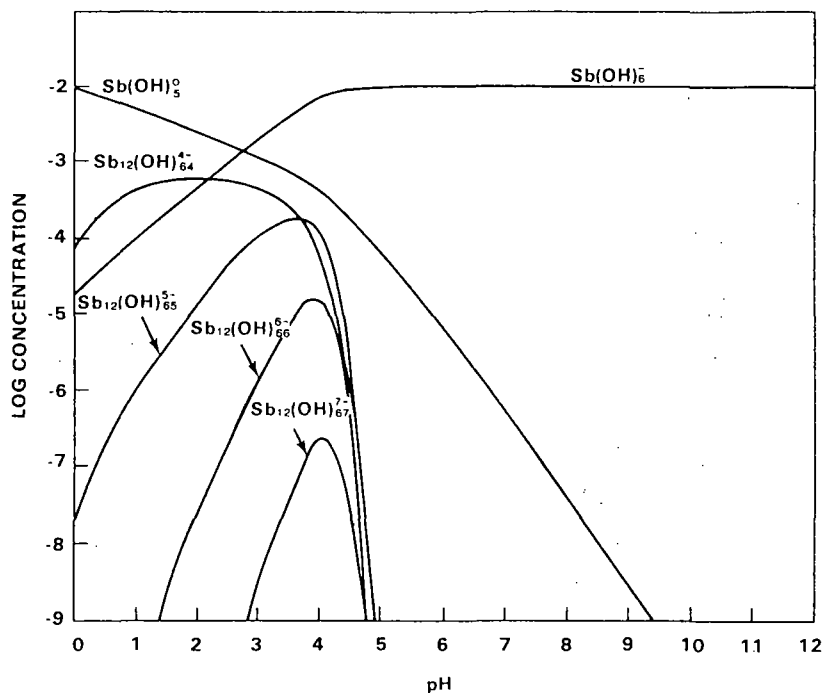


Figure 4-4. The concentration of Sb(V) species in equilibrium with 0.01 M total Sb(V).

which the concentration of the dominant solution species in equilibrium with the least soluble Sb solid phase is plotted as a function of $pe + pH$. The solids are highly soluble in environments with redox potentials greater than $pe + pH$ of 10. Even at $pe + pH < 10$, the solubility of Sb_2O_3 is fairly high ($10^{-4.2}$ M). The antimony-sulfide solid, Sb_2S_3 , will not likely form because the S^{2-} concentrations necessary to precipitate the solid will also form very high concentrations of the solution species $Sb_2S_4^{2-}$.

PRECIPITATION/DISSOLUTION

Although very limited literature is available for Sb behavior in the environment, all of the known Sb solids are fairly soluble. Thus, it appears that Sb concentrations in geologic environments may primarily be controlled by adsorption/desorption reactions rather than precipitation/dissolution.

ADSORPTION/DESORPTION

Little is known of the adsorptive behavior of Sb in soil, subsoil, or ground water, though preliminary studies suggest it is a mobile constituent under diverse environmental conditions (Shvartsev et al. 1974; Ames and Rai 1979). Antimony has been

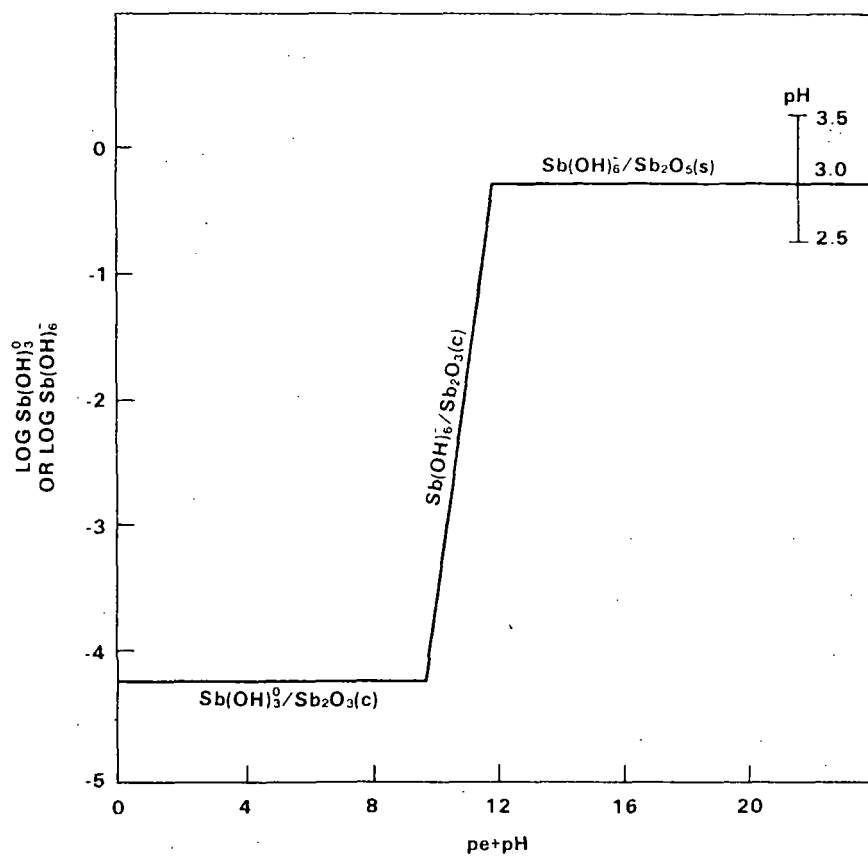


Figure 4-5. The effects of redox potential ($pe + pH$) on the solubility of $Sb_2O_3(c)$ and $Sb_2O_5(s)$ and the nature of dominant aqueous species.

used as an indicator species in hydrogeochemical prospecting because of its high mobility in various geochemical settings from oxygenated to highly reduced waters (Shvartsev et al. 1974). The two valence states [Sb(III), Sb(V)] are found primarily in solution as neutral and negatively charged species $[Sb(OH)_3^0]$, $[Sb(OH)_6^-]$ over the pH range of about 3 to 12 (Figure 4-1). Low adsorption (K_d) is observed in soil from high salt, high pH solutions (Ames and Rai 1979).

Migration has been rapid through soils following spillage of nuclear fuel reprocessing wastes (Haney and Linderoth 1959, Haney 1967, Magno et al. 1970). Adsorption may become more significant under weakly acidic (pH 4 to 5.5) soil/subsoil or ground water conditions where amphoteric hydrous oxides are positively charged, encouraging adsorption of anionic Sb components. Considerable research is needed to define the magnitude of Sb adsorption from utility waste leachates under diverse subsurface conditions.

Chemical Attenuation Rates, Coefficients, and
Constants in Leachate Migration
Volume 1: A Critical Review

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5. ANTIMONY

5.1 Statement of Probable Fate

The fate of antimony in the aquatic environment is determined by a number of factors including pH, Eh, sorptive interactions, and biologically mediated methylation. Due to the relatively high solubility of the antimonite and antimonate ions, most of the antimony introduced into the aquatic environment is probably transported in solution to the oceans. Coprecipitation with iron and aluminum oxides, adsorption by mineral surfaces, and bioaccumulation may, however, be responsible for removing some antimony from solution. Biologically mediated methylation or reduction to stibine (SbH_3) may occur in reducing environments, resulting in remobilization of antimony. The relative importance of each of these processes varies widely among watersheds; but, in general, transport of dissolved antimony to the oceans is the most probable dominant fate.

5.2 Identification - Geochemistry of Antimony

Antimony is an element occurring in concentrations of about 0.2-0.5 ppm in the earth's crust (A.D. Little, Inc. 1976). Important minerals of antimony are the native element Sb; stibnite Sb_2S_3 ; kermesite $\text{Sb}_2\text{S}_2\text{O}$; senarmonite, Sb_2O_3 ; jamesonite, $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$; boulangerite $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$; and the sulfantimonides of copper, silver, and nickel. Important artificial compounds include stibine, SbH_3 (a noxious poisonous gas), the chlorides SbCl_3 and SbCl_5 , the sulfides Sb_2S_3 and Sb_2S_5 , and the oxides Sb_2O_3 and Sb_2O_5 .

Antimony has chalcophilic properties, and thus combines readily with sulfides. Antimony shows no marked preference for mafic or silicic rocks. Antimony becomes enriched in the early stages of magmatic differentiation in sulfide bodies. In addition, antimony accumulates in late-stage granitic pegmatites, together with niobium and tantalum oxides, in granodiorites, and hydrothermal sulfide deposits. Antimony is also present in galena (a lead ore), in amounts up to 1%, where it replaces either the lead or the sulfur. Antimony may also substitute for arsenic in many minerals.

Little is known about the behavior of antimony during weathering. The antimony sulfides may be converted to the corresponding oxides, and it probably occurs in both hydrolysate and oxidate sediments. Antimony may accumulate with heavy elements in carbonaceous shales or become sorbed on clays and hydrous oxides. Thus, it may be enriched in manganese oxide sediments and black shales.

Antimony has an atomic number of 51 and an atomic weight of 121.75. In its compounds, it has a valence of +5, +3, or -3. When in the +3 state it has metallic characteristics. Antimony's chemical properties are analogous to those of arsenic, which is directly above it in the periodic table, and forms compounds with a number of other elements, such as oxygen, hydrogen, sulfur, and the halogens (Weast 1977).

Antimony's CAS number is 7440-36-0; its TSL number is A167-6664.

5.3 Summary of Fate Data

5.3.1 Photolysis

Antimony compounds may undergo photochemical reactions, but none of these appear to be important in determining aquatic fate. Stibine (SbH_3) reacts with sulfur at 100°C in the presence of light to form antimony sulfide. Under the same conditions, stibine reacts with selenium to form antimony selenide (A.D. Little, Inc. 1976). Antimony trioxide can act as a photocatalyst for the oxidation of organic matter by ultraviolet light, producing organic peroxides (Markham et al. 1958.)

5.3.2 Chemical Speciation

The chemical properties of antimony resemble those of bismuth and arsenic. Antimony loses its 2(s) and 3(p) electrons readily, and may exist in the oxidation states -3, +3, +5, and 0, although the existence of simple Sb^{+3} or Sb^{+5} ions is improbable. In reducing environments, stibine (SbH_3) may be formed. Stibine is a gas at room temperature, and it is quite soluble in water (5,000 mg/l). It is not stable in aerobic waters and is hydrolyzed to form the oxide. The formation of stibine in bed sediments (which usually offer a reducing environment) may result in remobilization of antimony which had been removed from solution by adsorption, coprecipitation, etc.

Under moderately oxidizing conditions, antimony has a valence of +3, and it is found in solution as the hydrated trioxide, $\text{Sb}_2\text{O}_3(\text{H}_2\text{O})_n$. Unlike arsenic, which forms arsenious acid (H_3AsO_3) under mildly oxidizing conditions, the lower valence acid of antimony is unknown; however, the antimonites are well defined salts (Cotton and Wilkinson 1972). The higher acid, H_3SbO_4 , does exist, although it does not appear to dissociate completely to the SbO_4^{-3} ion even in the most alkaline conditions (Cotton and Wilkinson 1972). This form of antimony, in which the element exhibits a valence of +5, is found only in highly oxidizing environments.

Antimony salts, added to aqueous media, are hydrolyzed to the oxide or antimonite acid forms. Although the hydrolysis products are usually less soluble than the original salts, the solubility is still sufficient to keep antimony in solution, except for cases of extremely heavy loading. When the system is no longer saturated, any antimony that precipitated out as the oxide will go back into solution.

The oxides, i.e., antimonite and antimonate forms, which are stable in the redox range typically observed in natural waters, all have sufficient solubility to keep antimony in solution at the levels of concentration normally found in natural waters. The calcium, magnesium, and sodium salts of the antimonates and antimonites are probably not a significant control on antimony solubility; but, by analogy to arsenic, some of the trace metal compounds may exhibit limited solubility. Thus, one could speculate that the presence of heavy metals (e.g., copper) in solution may reduce the mobility of antimony.

5.3.3 Volatilization

Antimony may be volatilized when in the form of stibine or its methylated derivatives. Stibine can be formed by reduction of antimony in the sediments. Although biomethylation of antimony has not been demonstrated, there are no obvious thermodynamic or kinetic obstacles (Parris and Brinkman 1975, 1976). Moreover, the elements Sn, Pb, As, Se, Te, which surround antimony in the periodic table, are subject to biomethylation, suggesting that biomethylation pathways could exist for antimony (Parris and Brinkman 1975, 1976). Stibine is rapidly oxidized in air or oxic water to form Sb_2O_3 . It is likely then, that most of the stibine formed in the sediments reacts in the water column to produce the oxide, resulting in remobilization of antimony.

The methylated forms of antimony are also subject to oxidation. Parris and Brinkman (1976) estimate the rate of oxidation of trimethylstibine as greater than $10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. The product of this reaction, $(\text{CH}_3)_3\text{SbO}$, is much more soluble than trimethylstibine; and, therefore, this oxidation would probably tend to reduce volatility. The rapid rate of oxidation implies that, if trimethylstibine is formed in natural systems, much of it would be oxidized before it volatilized and only a small amount of the volatile antimony compounds formed by either abiotic or biotic mechanisms would be liberated to the atmosphere.

5.3.4 Sorption

The extent to which sorption reduces the aqueous transport of antimony is unknown, but it is clear that sorption processes are normally the most important mechanisms resulting in the removal of antimony from solution. Antimony apparently has an affinity for clay and other mineral

surfaces. Coprecipitation of antimony with hydrous iron, manganese, and aluminum oxides may exert a significant control on antimony mobility in areas where there is active precipitation of these metals. Crecelius et al. (1975) studied the metal concentrations of Puget Sound, Washington, and found that, in uncontaminated areas, most of the antimony in the sediments was bound to extractable iron and aluminum compounds. Antimony bound in such forms would probably be susceptible to remobilization via bioaccumulation, reduction, or biomethylation. On the other hand, antimony in heavily contaminated areas was found mainly in stable, unextractable forms. These forms might include the oxide or insoluble metal antimonates or antimonites. Crecelius et al. (1975) found that less than 10% of the antimony in sediments from both the contaminated and uncontaminated sediments was bound to easily oxidizable organic matter. Since antimony has an anionic character in aqueous solution, it probably has little affinity for complexation with humic and fulvic acids, which are important complexing agents for metals.

Maxfield et al. (1974), in their study of heavy metals in the Coeur d' Alene River of Idaho, found that antimony was concentrated and evenly distributed throughout the sediment. They suggested that, although antimony is being adsorbed by all types of particulate matter, it is not being strongly bound in the sediments. The high levels of antimony that are characteristic of this region are due to former antimony mining activities; and the antimony found in the sediments probably entered the system, not in the dissolved state, but rather on particulate matter. Maxfield et al. (1974) concluded that the results suggest that antimony is leaving the sediments; but since this is a diffusion controlled process, it proceeds slowly.

Strohal et al. (1975) investigated antimony in the sediments of the North Adriatic Sea. They found that the fixation rate of antimony on various inorganic particles is rather small. They found, however, that antimony could be accumulated by organic matter, especially humic acids. Unfortunately, sorption processes of antimony have not been studied in enough detail to quantify the role of sorption in its aquatic fate.

5.3.5 Bioaccumulation

Antimony is only slightly bioaccumulated and has been little studied in aquatic organisms. Leatherland et al. (1973) found low levels of antimony in various fishes and invertebrates collected off the northwest coast of Africa; antimony was generally present in higher concentrations in invertebrates than in fish. Aquatic organisms from the Danube River and Danube Canal in Vienna, Austria, were found to contain only background

levels of antimony (Rehboldt et al. 1975). Similar results were obtained in clams, mussels, and shrimp by Bertine and Goldberg (1972). Table 5-1 summarizes known bioconcentration factors for antimony.

Table 5-1
Bioconcentration Factors for Antimony

<u>Taxon</u>	<u>Bioconcentration Factor^a</u>	<u>Reference</u>
Freshwater fish	40	Chapman <u>et al.</u> 1968
Freshwater invertebrates	16,000	Chapman <u>et al.</u> 1968
Marine fish	40	Chapman <u>et al.</u> 1968
Marine invertebrates	16,000	Chapman <u>et al.</u> 1968

- a. Concentration factors are defined by the ratio of the concentration of the element in the organism in ppm (wet weight) divided by the concentration of the element in water (ppm).

5.3.6 Biotransformation

It has been reported that a species of bacteria, Stibiobacter senarmontii, utilizes the energy released by metabolically induced oxidation of antimony (Lyalikova 1974), but the distribution and ecological importance of this organism is unknown. As previously mentioned, biomethylation of antimony has not been demonstrated, but it is thought that this process could occur in the environment (Parris and Brinkman 1976).

5.4 Data Summary

Although the aquatic fate of antimony has not been comprehensively studied, it appears that most of the antimony introduced into aquatic environments is probably transported in solution to the oceans. Sorption processes act as temporary sinks for antimony, but bioaccumulation, reduction to stibine, and possibly biomethylation may act to remobilize antimony in bed sediments. There is a possibility that heavy metals in solution could react with antimonite (H_3SbO_3 , H_2SbO_3^- , HSbO_3^{2-} , SbO_3^{3-}) or antimonate (H_3SbO_4 , H_2SbO_4^- , HSbO_4^{2-}) species to form insoluble compounds, greatly reducing the mobility of antimony, but the importance of such reactions is unknown. The aquatic fate of antimony is summarized in Table 5-2.

Table 5-2
Summary of Aquatic Fate of Antimony

<u>Environmental Process</u>	<u>Summary Statement</u>	<u>Confidence of Data</u>
Photolysis	Not important.	Low
Chemical Speciation ^a	Antimony is present as the soluble oxide or antimonite salt in most natural waters. In reducing environments, volatile SbH_3 may be formed. Most species of antimony are soluble and mobile in the aquatic environment.	Medium
Volatilization	Important where SbH_3 is stable.	Medium
Sorption ^a	Antimony is adsorbed by clays and organic materials.	Low
Bioaccumulation	Very slight.	Medium
Biotransformation ^a	Biomethylation may occur.	Low

-
- a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

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WATER-RELATED ENVIRONMENTAL FATE OF
129 PRIORITY POLLUTANTS

Volume I:

Introduction and Technical Background, Metals and Inorganics,
Pesticides and PCBs

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Vulnerability of soil and groundwater to pollutants

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INFLUENCE OF ACIDIFICATION ON THE CONCENTRATION OF LESS
COMMON TRACE ELEMENTS IN DUTCH GROUNDWATER

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ABSTRACT

Thirty six rare trace elements were measured in groundwater at 31 locations in the Netherlands. Especially in sandy soils with a low pH, relatively high values of some metals are found, while concentrations of trace anionic species like As are decreasing.

1. INTRODUCTION

Knowledge of background levels of trace elements in groundwater is important as a reference in pollution events and in the assessment of groundwater acidification.

Little information is available on a number of less common elements in Dutch groundwater. This relates to their background concentrations, the variation in concentration and the dependence of element concentrations on soil type and groundwater pH.

In this work less common elements in Dutch groundwater have been analyzed in relation to soil type. Concentrations are presented as a function of pH, which gives an indication of the consequences of acidification, especially in sandy soils. Elements measured are: Ag, Al, As, Ba, Br, Cl, Co, Cr, Cs, Eu, Hf, Hg, J, Mn, Mo, Ni, Rb, Sb, Sc, Se, Sr, Th, U, V, W, Zn and at some locations: Au, Ce, La, Lu, Nd, Sm, Sn, Ta, Tb, Yb.

2. SAMPLING AND ANALYSIS

Sampling stations were selected from the national groundwater quality network of the National Institute of Public Health and Environmental Hygiene [1], figure 1.

At 31 location samples were taken at 10 m and 25 m depth using a vacuum pump system in order to minimize contamination [2]. A small sample was used for on-site pH-measurements. Analysis of trace elements requires special precautions to avoid contamination from sampling materials or particulate suspended matter. Immediately after collection the sample is filtered under nitrogen through a 0.45 μm membrane-filter using a full-teflon filtration apparatus [3], and subsequently acidified with HNO_3 to pH 2.

In comparison with common practise to collect unfiltered samples the difference in final results is obvious. For La, for example, the concentration in groundwater ususally is less than 100 ppt. The concentration in clay is about 45 ppm [4]. Assuming that per liter 5 mg of suspended particulate matter is dissolved by acidification to pH=2, this would lead to an incorrect dissolved concentration of 225 ppb La. Other elements showing a similar behaviour are Ce, Co, Eu, Hf, Lu, Sc, Sm, Ta, Ti and Th.

In our laboratory, neutron activation analysis was used after a pre-concentration procedure, which has been applied in the determination of trace elements in sea water [5-8].

3. RESULTS

Average values of the measured elements are listed in table 1, divided into three pH-ranges and two sampling depths. In this table no distinction is made according to soil type.

Average pH-values in groundwater of three soil types clay, sand and peat are given in tabel 2. Especially under sandy soils a fairly wide pH-range has been observed. Low pH-values are measured under sand in the south of the Netherlands (pH = 3.8) in an area sensitive to soil and groundwater acidification.

In table 3, the concentrations of some important elements are given according to soil type and pH. As there is only a limited amount of samples in each group, the values show a great variation.

The effect of increasing acidification of groundwater on the concentrations of less common elements in groundwater can be deduced from figures 2-5. Europium is an example of an element which is dissolved in acidic groundwater. Other elements behaving similarly are Co, Ni, Cr^{III}, Zn, Sc and lanthanides. According to the results for Zn and Ni based on sampling of all 370 measuring points of the national groundwater quality network, highest concentrations and variations can be found in groundwater under sandy soils. Probably this is caused by wide pH ranges in and low cation exchange capacity of sandy soils. Aluminium shows a minimum in dissolved concentration at pH ~ 5.5, which is in agreement with the minimum solubility of Al phases at this pH [9]. Extremely high Al-concentrations can be found around a pH-value of about 4.

Many trace oxy-anions like As, Mo or W show decreasing concentrations with increasing acidification. In this scope also the redox can be of importance, for example the reduced form As^{III} is more soluble. The As concentration may increase in reducing environments [10], particularly in deeper groundwater.

Element correlation studies have shown a striking correlation of vanadium with total organic carbon. An explanation might be found in the combustion of oil, as oil ash may contain considerable amounts of vanadium (~ 5%) [11]. According to Pacyna [12] the atmospheric deposition of vanadium through oil firing is considerable.

Moreover, relatively high V concentrations (up to 100 ppb) have been observed in rainwater, particularly in the more industrialized western part of the Netherlands [13]. The mobility of the oxyanion vanadium in soil is higher than that of trace metals, like Cu and Zn, which carry a greater potential for further dispersion into deeper groundwater. We did not measure sufficient locations to completely exclude dependence of vanadium concentration on soil type. Here further research is needed. Solubility relations are found for Ba and SO₄, for Sr and CO₃ and for U and CO₃. High concentrations of the cation are only possible in water with low concentrations of the anion.

4. CONCLUSIONS

The limited number of data can already give an indication of the consequences of increasing acidification of groundwater in the province of North Brabant and Drenthe, as described in the contribution of W. van Duijvenbooden [14]. It shows that the concentrations of heavy metals like Zn, Co and Ni and also Al will increase with decreasing pH, while anions like Mo or As will decrease in concentration. As a result, an essential anionic trace element like Mo, might not be available in necessary concentrations for plants, leading to plant damage. More research is needed on the influence of acidification on trace element concentrations in groundwater in different soil types. On the other hand very high Al-concentrations may cause troubles in case of drainage of groundwater to surface waters.

Information on the chemical form of trace elements in groundwater is important for a correct description of the behaviour of trace pollutants. Speciation techniques are available, but speciation has to be done in the field immediately after sample collection which requires the use of field laboratories. In this respect more information on the redox state of the sampled groundwater is required.

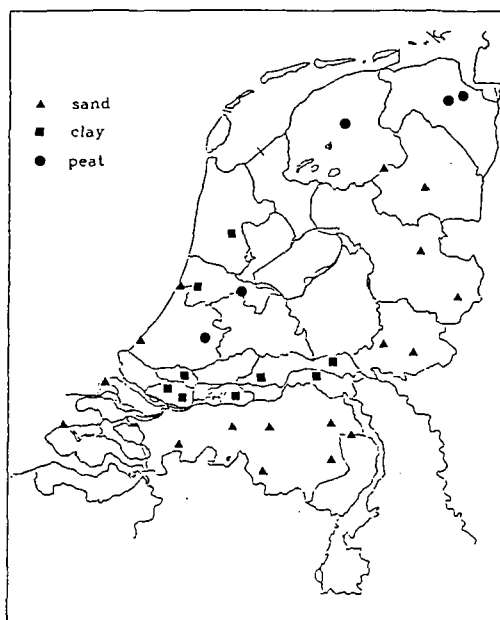


Figure 1: Sampling stations for groundwater on different soil types.

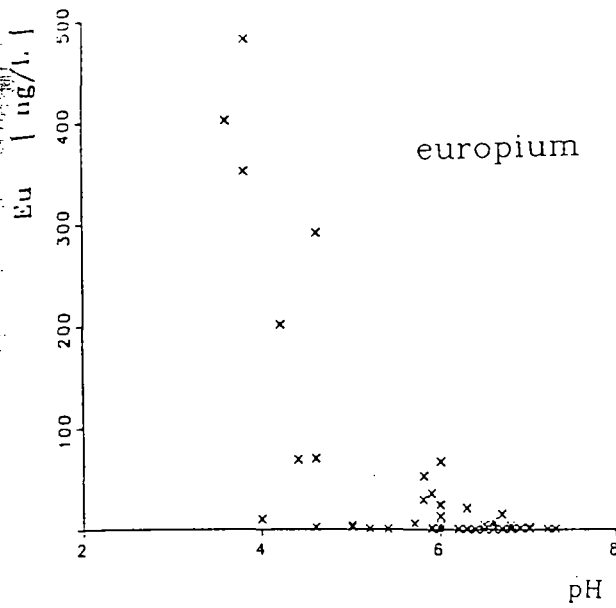


Figure 2: Europium concentrations
in groundwater

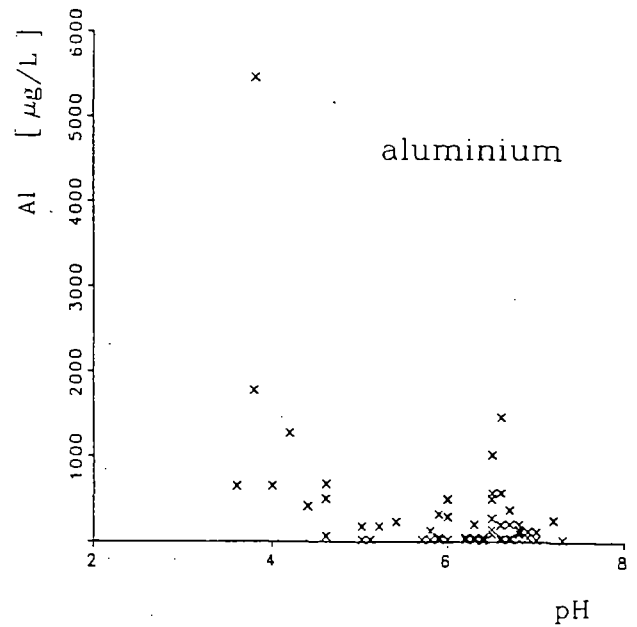


Figure 3: Aluminium concentrations
in groundwater

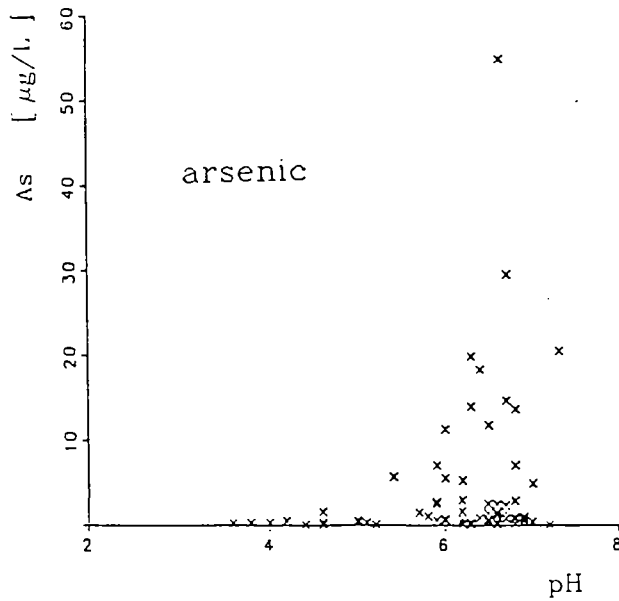


Figure 4: Arsenic concentrations
in groundwater

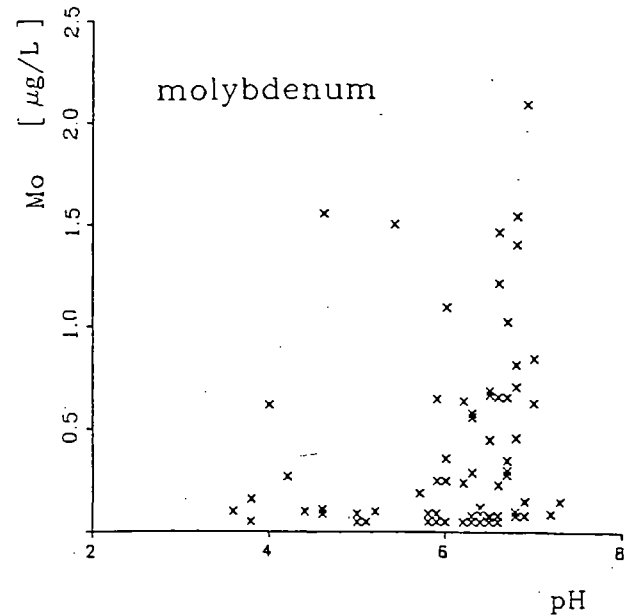


Figure 5: Molybdenum concentrations
in groundwater

Table 1. Average concentration of Dutch groundwater in ppb for three pH-ranges and two depths (10 m and 25 m). *ug/L*

Ele- ment	pH 3,6-5		pH 5-6		pH 6-7		range
	10 m	25 m	10 m	25 m	10 m	25 m	
Al	1834	410	70	206	69	290	<20-5460
As	0.31	0.43	2.0	0.9	3.0	4.6	<0.01-55
Co	4.9	4.4	0.3	0.21	0.16	0.15	0.01-19.3
Cr ^{IV}	0.55	0.53	0.7	0.61	0.65	0.83	0.03-9.76
Eu	0.21	0.138	0.016	0.021	0.004	0.005	<0.005-4
Hg	0.026	0.014	0.02	0.019	0.018	0.019	0.01-0.05
La	max91	max105	max2.1	<0.1	<0.1	<0.1	<0.1-105
Mn	300	197	436	510	440	430	5-2060
Mo	0.23	0.34	0.14	0.14	0.44	0.47	<0.05-2.1
Ni	16.9	2.4	2.9	0.9	2.9	1.2	0.2-36.7
Sb	0.32	0.04	0.05	0.031	0.06	0.042	<0.02-1.33
Sc	0.15	0.25	0.087	0.069	0.031	0.052	0.05-0.84
Se	0.014	0.011	0.034	0.009	0.012	0.008	<0.005-0.179
Sr	609	365	800	970	870	1549	80-6050
U	0.43	0.29	0.16	0.02	0.11	0.04	<0.01-1.3
V	0.76	0.57	1.2	0.72	0.84	0.83	0.06-3.44
W	0.019	0.035	0.5	0.08	0.18	0.22	<0.015-3.64
Zn	102	53	85	7	23	4.1	<1-440

Table 2. pH in Dutch groundwater for different soil types.

soil type	clay	sand	peat
mean pH	6.4	5.7	6.1
standard deviation	0.3	1.2	0.3
number of samples	9	17	5

Table 3. Average concentrations of selected elements (ppb) for different soil types at 10 m depth.

pH-range	clay		sand			peat	
	5-6	>6-7	<5	5-6	>6-7	5-6	>6
Al	<50	38	2300	<20	41	200	113
As	6.2	3.2	0.3	0.66	3.15	0.87	2.7
Co	0.27	0.16	6.20	0.29	0.15	0.40	0.16
Eu	0.013	0.006	0.260	0.004	0.003	0.032	0.007
Mo	<0.05	0.46	0.27	0.10	0.59	0.35	<0.05

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CHEMICAL CHARACTERISTICS OF LEACHATE FROM MUNICIPAL SOLID WASTE LANDFILLS IN WISCONSIN

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Abstract

Collection and treatment of leachate from landfills has been practiced in Wisconsin for many years. During this time, numerous measurements have been made of leachate quality to determine the degree of waste stabilization, parameters of potential concern with regard to groundwater contamination, leachate treatability and treatment billing costs.

Leachate quality data from 16 active municipal solid waste landfills, some of which have practiced co-disposal of hazardous wastes, is compiled and analyzed. Parameters summarized include pH, suspended solids, specific conductance, BOD, COD, hardness, alkalinity, sulfates, chlorides, numerous metals and priority pollutants.

Data analysis includes time - concentration graphs for select parameters, determination of the range and median value for each parameter for individual sites and histograms displaying the frequency of occurrence of site medians for each parameter. Leachate chemical characteristics are compared to that of typical municipal wastewater and water quality standards.

The analysis confirms that leachates from municipal solid waste landfills in Wisconsin are severely contaminated liquids with a strength greater than or equal to that of municipal wastewater for most parameters measured and several contaminants exceeding drinking water standards. A significant degree of variability is also encountered and factors which may be influencing leachate quality at the individual sites are identified and discussed.

Introduction

Municipal solid wastes are wastes generated primarily by residential activities but usually also include varying amounts of commercial and industrial wastes, some of which may be classified as hazardous. These wastes include a wide variety of

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discarded materials such as paper products, food wastes, garden wastes, glass and ceramics, various metals, plastic, wood, ash and dirt. Some industrial process solid wastes that often are disposed of in municipal solid waste landfills include papermill sludges, boiler ash and foundry sands. When landfilled in a humid climate like Wisconsin's these wastes begin to decompose and leach. Sources of liquids which contribute to this leaching action can be percolating rainfall and surface water, infiltrating groundwater or the refuse itself. The resultant liquid called municipal solid waste (MSW) leachate can be severely contaminated making it undesirable from both an aesthetic and toxicological viewpoint.

The chemical composition of MSW leachate has been described by ranges in the literature which, while indicative of the variability, give little insight into the likely composition of a "typical" leachate in Wisconsin. The development and review of treatment proposals for MSW leachate are dependent on adequate characterization of leachate quality. Further knowledge of its chemical contamination potential is also necessary to insure adequate groundwater protection in the design of landfills. To help fill this gap, leachate quality information from several Wisconsin landfills has been gathered and analyzed. This summary is not intended to be the final answer to prediction of MSW leachate quality, but hopefully, when examined with other information available in the literature and with regard to site specific variables, a more accurate assessment of a given site's expected leachate chemical characteristics will be possible.

Methods

To initiate this study, several MSW landfills with leachate collection systems were identified through discussions with Department of Natural Resources Solid waste staff. Department files were then examined and available data on leachate characteristics was compiled. Where necessary, supplemental data was obtained through follow-up contacts with landfill operators and the wastewater treatment plants treating leachate. Figure 1 is a map of Wisconsin showing the approximate location of those sites where leachate data has been obtained. The numbers identifying sites on this map and throughout this paper are the license identification numbers used by the Department in its records. Additional information on each site is summarized in table 1. From this table, it should be noted that all of these sites are relatively young so that the leachate data compiled in this paper is representative of MSW landfills in their early stages of decomposition.

Only data from leachate collection systems and leachate headwells has been included in this paper. These sample locations were selected because they were felt to be more representative of "true" leachate than leachate seeps, ponds and contaminated groundwater monitoring wells.

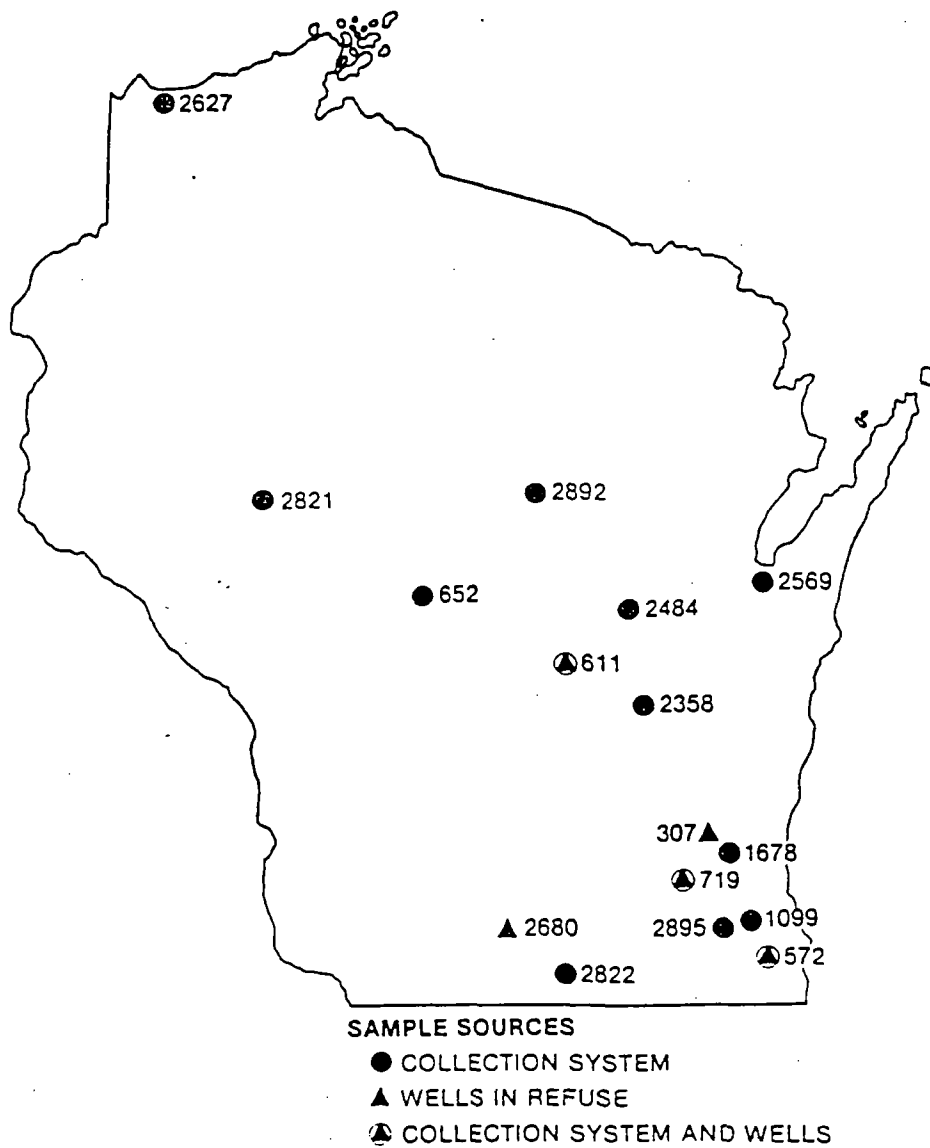


FIGURE 1: LOCATION OF MSW LANDFILLS INCLUDED IN THIS REPORT

TABLE 1: Characteristics of MSW Landfills Included in This Report

License #	Name	Total Design Volume (CY)	Principal Waste Types Received	Type of Design	Leachate Collection System			Date Filling Began	% Design Volume Filled	Leachate Treatment Method	Sample Location
					None	Part.	Full				
307	WMI-Polk	0.5x10 ⁶	MSW	Clay Lined	X			1970	100%(2)	None	Headwell
572	Land Reclamation LTD	9.5x10 ⁶	MSW, IND, HW	Zone of Saturation		X		Pre 1970	50%	Racine STP	Collection System
611	Winnebago Co.	4x10 ⁶	MSW, IND	Zone of Saturation			X	Pre 1970	75%	Oshkosh STP	Collection System
652	Tork	1.5x10 ⁶	MSW, IND	Cut Off Wall		X		1970	90%	Wisconsin Rapids STP	Collection System
719	Delafield (lined area only)	1x10 ⁶	MSW	Clay Lined			X	1975	90%	Delahart STP	Headwells Collection System
1099	WMI-Franklin	9x10 ⁶	MSW, IND, HW	Zone of Saturation		X		Pre 1970	25%	Milwaukee MSD	Collection System
1678	WMI-Omega Mills (North)	10x10 ⁶	MSW, IND, HW	Zone of Saturation		X		1971	80%	Milwaukee MSD	Collection System
2358	Fond du Lac Co. (Area II)	0.5x10 ⁶	MSW, IND	Zone of Saturation			X	1978	75%	Fond du Lac STP	Collection System
2404	Outagamie Co. (pre-expansion)	2x10 ⁶	MSW, IND	Zone of Saturation			X	1975	95%	Appleton STP	Collection System
2569	Brown County East	6x10 ⁶	MSW	Clay Lined			X	1976	20%	Green Bay MSD	Collection System
2627	Superior (Moccasin Mike)	0.6x10 ⁶	MSW	Zone of Saturation			X	1976	60%	Superior STP	Collection System
2630	Dane Co. (Verona)	1.5x10 ⁶	MSW	Natural Attenuation		X		1977	70%	None	Headwell
2822	Janesville	0.7x10 ⁶	MSW, IND	Clay Lined			X	1978	50%	Janesville STP	Collection System
2821	Eau Claire Co. (7 Mile Creek)	1.2x10 ⁶	MSW	Clay Lined			X	1978	30%	Eau Claire STP	Collection System
2892	Marathon Co.	1.5x10 ⁶	MSW, IND	Clay Lined			X	1980	20%	Weyerhaeuser WWP	Collection System
2895	WMI-Muskego (Lined Area Only)	1.3x10 ⁶	MSW	Clay Lined			X	1980	40%	Milwaukee MSD	Collection System

(1)MSW = Municipal Solid Waste; IND = Non Hazardous Industrial Waste; HW = Hazardous Waste
 (2)Presently Closed

Samples from leachate collection systems have the advantage of being representative of leachate that is actually extracted from a site for treatment. These are typically a single location such as a manhole or collection tank where all leachate within the site is directed to for removal. It is usually at this location where a sample would be collected for analysis. A second option would be to collect a sample from a truck at the time of delivery of the leachate to a treatment plant (if by truck). No distinction between these sampling locations is made in this report nor it is felt this difference is significant unless the leachate is stored for extended periods of time prior to sampling.

Some sites extract leachate from several manholes, each connected to collection systems draining different portions of the landfill. In these instances, the leachate characteristics may vary considerably from manhole to manhole.

Leachate head wells are monitoring wells that have been specifically installed to monitor the leachate head level and quality within a site. For sites without functioning leachate collection systems this is the only way of obtaining a sample of leachate for analysis. For some sites both leachate collection system and headwell samples were available. An important distinction between leachate headwells and contaminated groundwater monitoring wells is that the headwells are developed within refuse, not in underlying soils or adjacent to the site. Thus, these wells should be obtaining a leachate sample that has not been subject to groundwater dilution or otherwise attenuated by soils underlying the site.

Most of the leachate analyses summarized in this report are of samples that were retrieved by the site operator or their consultant so the exact method of sampling is often not known. Most samples were probably retrieved by dipping a PVC bailer into the manhole, tank or headwell and transferring the sample to one or more bottles for transport to a lab for analysis. Ph and conductivity are usually measured in the field on an unfiltered sample. Some samples have been filtered in the field prior to preservation but a majority appear to have been preserved and analyzed without filtering. These inconsistent procedures have undoubtedly contributed to the variability of the data although this is more of a problem for parameters which are very sensitive to sampling methodology (e.g. iron) than for others.

Once collected, the samples have been taken to different labs for analysis. Although not reported, it is expected most labs followed accepted procedures for analyses such as "Standard Methods for the Examination of Water and Wastewater" (1976). Since alternative analysis procedures are available, the variability in these results may be partially attributed to some labs using different methods. A range in detection limits because of this complicates further analysis of the data, particularly for trace contaminants.

In spite of these limitations it is felt the data summarized in this report is of reasonably good quality. Although it may not be equally precise it does provide a good indication of these MSW leachate characteristics, particularly where multiple analyses are available.

Results

Table 2 summarizes the analytical results for each parameter tested. Included are the total number of samples tested, the overall range of values encountered, a best estimate for the range within which most values fell and, for comparison, the overall range of values reported in this literature by several sources. The Wisconsin data includes analyses of samples from both collection systems and headwells. A brief discussion of each parameter follows along with presentation of site range and median values and time-concentration graphs for select parameters. To accommodate large variations in contaminant concentrations a logarithmic range scale was used for the range graphs of many parameters. Where this scale was exceeded the highest values are indicated on the graph. The median values from each site are presented below the range graph in a histogram showing the frequency of occurrence within a concentration range.

pH

The pH data from 12 Wisconsin landfills is summarized in figure 2. Only data from collection systems was included as headwell data was infrequent and extremely variable.

From this figure it is apparent that significant variability exists between sites but median values fall within a relatively narrow range of 5.8 to 7.4 with most medians being slightly acidic. These acidic pH values are to be expected due to the abundance of volatile fatty acids and CO₂ within a MSW landfill.

These values are within the range reported in the literature for other MSW leachates although the extremes reported by some researchers were never witnessed.

It is suspected that the highly buffered nature of MSW leachate would tend to dampen variation and confine the pH of a site within a narrow range. The variability is best addressed by examining the pH data of one of the more closely monitored sites through time. The pH data as a function of time for site #652 is shown in figure 3. This plot shows that although the pH values can fluctuate over the entire range in several days, generally the daily and weekly fluctuations are a much smaller portion of this range. The changes in pH probably reflect subtle changes in fill metabolism or site conditions such as dilution by surface water or groundwater.

Table 2: Summary of Wisconsin MSW Leachate Chemical Characteristics

Parameters	No. of Values	Wisconsin MSW Leachates		Range Reported in the Literature (mg/l) (3)
		Overall Range (mg/l)	Typical Range (mg/l)	
-T. Alkalinity (as CaCO ₃)	50	4-10,630	500-10,000	0-20,850
-Aluminum	7	ND-85.0		0.5-41.8
-Antimony	23	ND-2.0	ND-2.0	NR
-Arsenic	34	ND-70.2	ND-0.4	ND-40
-Barium	9	ND-2.0	ND-1.0	ND-9.0
-Beryllium	23	ND-0.08	ND-0.08	ND
-BOD ₅	876	67-64,500	400-40,000	9-54,610
-Boron	2	4.6-5.1		0.42-70
-Cadmium	53	ND-0.40	ND-0.10	ND-1.16
-Calcium	7	200-2,100		6-7,200
-Chloride	98	2-5,590	100-2,500	5-4,350
-T. Chromium	42	ND-5.60	ND-1.0	ND-22.8
-Hex Chromium	3	ND		ND-0.06
-COD	108	62-97,900	500-50,000	0-89,520
-Conductivity (1)	352	480-24,000	1,000-20,000	2,810-16,800
-Copper	41	ND-3.56	ND-0.5	ND-9.9
-Cyanide	27	ND-0.40	ND-0.40	ND-0.08
-Fluoride	1	0.74		0.1-1.3
-Hardness (as CaCO ₃)	92	206-225,000	500-10,000	0-22,800
-Iron	88	0.06-1,500	ND-500	0.2-42,000
-Lead	46	ND-1.2	ND-1.2	ND-6.6
-Magnesium	7	120-780		12-15,600
-Manganese	19	ND-20.5	ND-10	0.06-678
-Mercury	24	ND-0.01	ND-0.005	ND-0.16
-Ammonia-N	28	ND-359	0-350	0-1,250
-TKN	32	2-1,850	25-1,500	
-NO ₂ & NO ₃ -N	36	ND-250	0-10	0-10.29
-Nickel	40	ND-3.3	ND-3.3	ND-1.7
-Phenol	20	0.48-112	2-20	0.17-6.6
-T. Phosphorus	92	0.16-53	0-10	0-130
-pH (2)	432	5.7-7.66	5.7-7.6	1.5-9.5
-Potassium	7	31-560		2-3,770
-Selenium	33	ND-0.038	ND-0.04	ND-0.45
-Silver	17	ND-0.196	ND-0.05	ND-0.24
-Sodium	20	33-1,240		0-8,000
-Thallium	24	ND-0.32	ND-0.3	NR
-Tin	3	0.08-0.16		NR
-TSS	812	5-18,800	100-1,000	6-3,670
-Sulfate	66	ND-1,800	50-1,500	0-84,000
-Zinc	38	ND-162	ND-75	0-1,000

(1) ucho/cm

(2) Standard Units

(3) Clark and Pliskin (1976), Chlan and DeWalle (1977), Uloth and Mavinic (1977), Myers et. al. (1980) and James (1977).

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Table 3: Priority Pollutant Organics Detected in MSW Leachates

Parameter (1)	No. of Samples Above D.L./Analyzed	FOR SITES WHERE DETECTED	
		Range (PPB)	Median (PPB)
Acid Organics (11)			
phenol	3*/5	221-5,790	293
4 nitrophenol	1/5	17	
pentachlorophenol	1/6	3	
Volatile Organics (32)			
methylene chloride	6/6	106-20,000	2,650
toluene	5/5	280-1,600	420
1,1 dichloroethane	3/5	510-8,300	570
trans 1,2 dichloroethane	3/5	96-2,200	1,300
ethyl benzene	3/5	100-250	150
chloroform	3*/6	14.8-1,300	71
1,2 dichloroethane	2*/5	13-11,000	
trichloroethane	2/5	160-600	
tetrachloroethane	2*/5	26-60	
chloromethane	1/5	170	
bromomethane	1/5	170	
vinyl chloride	1*/5	61	
chloroethane	1/5	170	
trichlorofluoromethane	1*/5	15	
1,1,1 trichloroethane	1/5	2,400	
1,2 dichloropropane	1*/5	54	
1,1,2 trichloroethane	1/5	500	
cis 1,3 dichloropropene	1*/5	18	
benzene	1*/5	19	
1,1,2,2, tetrachloroethane	1/5	210	
acrolein	1/5	270	
dichlorodifluoromethane	1/5	180	
bis (chloromethyl) ether	1/5	250	
Base-Neutral Organics (46)			
Bis (2-ethyl hexyl) phthalate	5*/5	34-150	110
diethyl phthalate	4*/5	43-300	175
dibutyl phthalate	3*/5	12-150	100
nitrobenzene	2*/5	40-120	
isophorone	2/5	4,000-16,000	
dimethyl phthalate	2*/5	30-55	
butyl benzyl phthalate	2/5	125-150	
naphthalene	1*/5	19	
Chlorinated Pesticides (19)			
deltamethrin	1/5	4.6	
PCBs (7)			
PCB-1016	1/5	2.8	

*Includes suspect value near detection limit.

(1) No. in parentheses represents total number of compounds analyzed in category.

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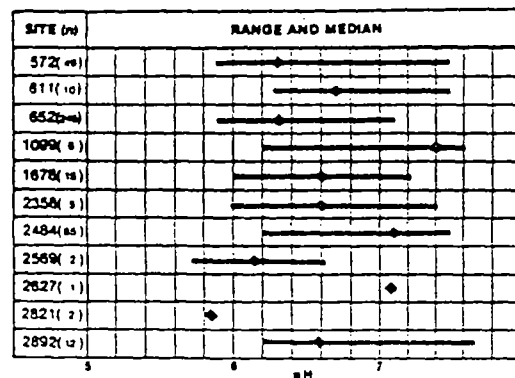
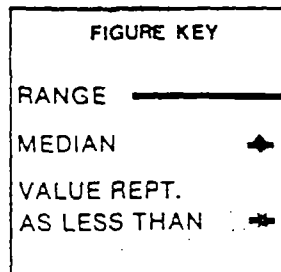


Figure 2. Site Ranges and Median Values for pH

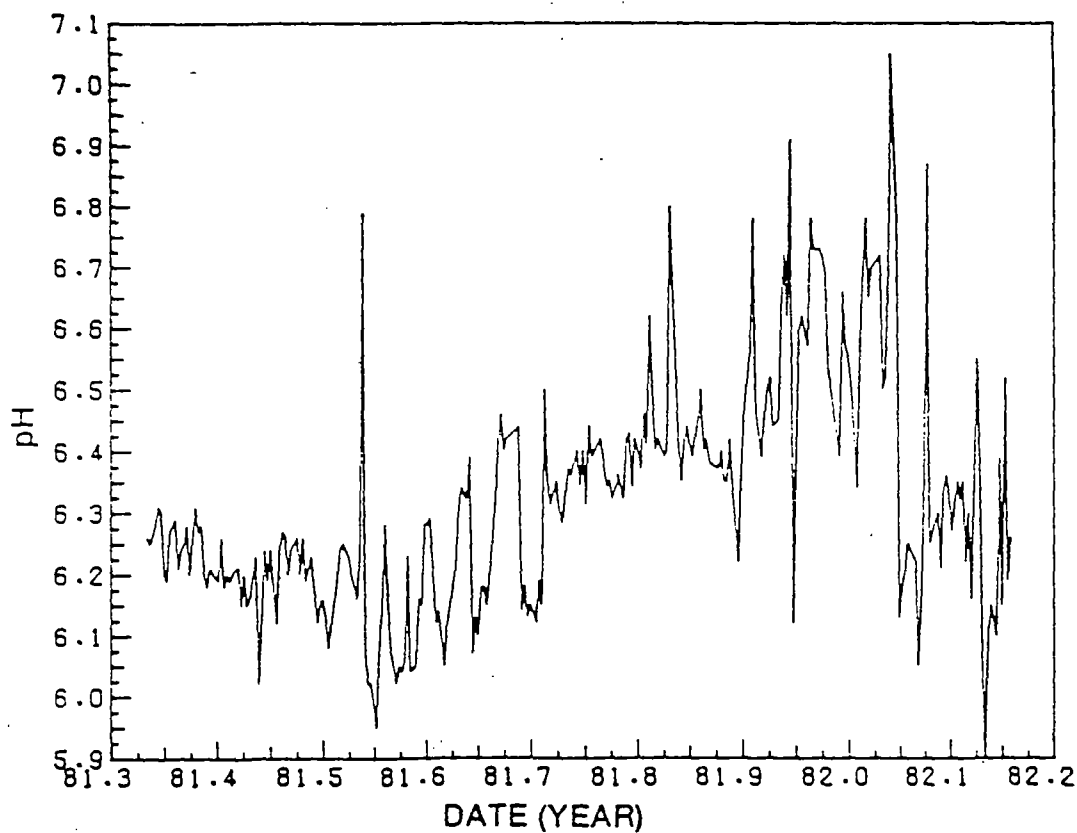


Figure 3 Leachate pH variations during one year at Site 652

Suspended Solids

The ranges and median values of suspended solids for 12 MSW landfill leachates are shown in figure 4. A majority of this data was compiled from sewage treatment plants which accept leachate for treatment since suspended solids are not typically used to assess groundwater impacts. Only data from collection systems has been presented because headwell analyses were not available for this parameter. As figure 4 demonstrates, the ranges of reported concentrations for suspended solids were quite broad for most sites reflecting a large degree of variability for this parameter. However, the median values exceeded 1,000 mg/l at only one site (2822) where only 2 values were reported. Median values were less than 500 mg/l for more than half the sites. These values are comparable to those reported in the literature for other MSW leachates.

The time variability of suspended solids is demonstrated by figure 5 which shows 12 months of weekly analyses for site #2895. The substantial fluctuation in these values demonstrates the difficulty in attempting to characterize a suspended solids concentration for MSW leachate in general or even that at a given site. While most values were 0-300 mg/l the possibility of values exceeding 1,000 mg/l cannot be discounted.

Aside from sampling and analytical error one would not expect to see a great deal of variability in MSW leachate suspended solids analysis due to the nature of leachate collection systems. Leachate collection pipes are usually surrounded by a granular medium for conducting leachate and providing bedding for the pipe. Although percolating leachate would be expected to flush some solids from the refuse, when the leachate passes through this medium a degree of filtering would be expected. One source of suspended solids may be surface water runoff which collects in the pipes prior to refuse deposition and is later washed through the system. Additional sources could include precipitation of ions, particularly iron, when the leachate is exposed to oxygen and flocs of biological growth which may build up in the collection system.

Total Dissolved Solids

Direct measurement of total dissolved solids (TDS) in MSW leachate is rarely performed in Wisconsin. Instead, since many of the soluble constituents in leachate are electrolytes, specific conductance is used as an indirect indication of dissolved solids. Based on limited samples from 3 landfills where simultaneous determinations of TDS and conductivity were done for MSW leachate in Wisconsin it would appear an approximate relationship between the two is as follows:

$$\text{TDS (mg/l)} = \text{specific conductance (umohs/cm)} \times (1-1.2)$$

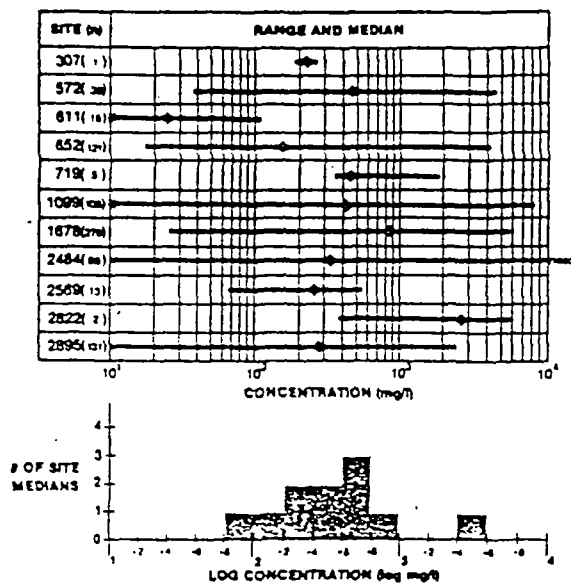


Figure 4 Site Ranges and Median Values for Total Suspended Solids

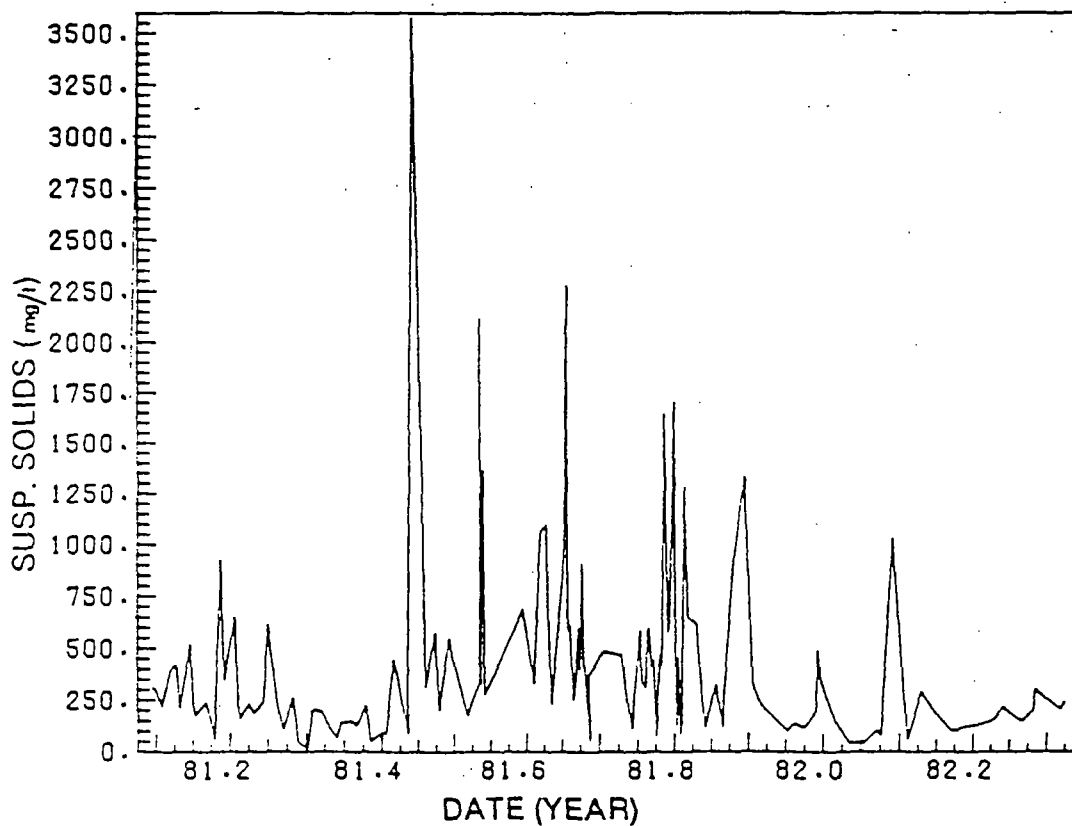


Figure 5 Leachate suspended solids over one year at Site 2895

This is in general agreement with the relationship reported by Standard Methods (1976) for polluted waters.

The conductivity ranges and median values for MSW leachate from 12 landfills are displayed in figure 6. This includes data from both leachate collection systems and headwells. From this figure it is evident these leachates contain a substantial quantity of dissolved solids with values for conductivity as high as 10,000 umhos/cm not uncommon. There is also a great deal of variability between sites. These values are comparable to those reported in the literature for other MSW leachates.

The individual site variability can best be addressed by examining a plot of conductivity vs. time as shown in figure 7 for site #652. Significant fluctuations are evident on a daily and seasonal basis. The seasonal peaks in the summer and winter months indicates this variability may be attributable in part to infiltration events flushing out varying amounts of dissolved constituents. Given the large daily variations it is apparent that detection of a pattern at any one site is dependent to some degree on the frequency of analysis. This variability, which exists on even a daily basis emphasizes the difficulty associated with predicting leachate quality.

Organics (BOD & COD)

The significant quantity of organic material in MSW leachate is reflected by its very high oxygen demand. The biochemical oxygen demand (BOD) test measures the oxygen depletion within a sample due to microbial activity and the chemical oxygen demand (COD) test uses a strong chemical oxidant. Not surprisingly, the COD is generally higher than the BOD, reflecting in part, the chemical oxidation of more recalcitrant organic compounds not subject to rapid biological utilization.

The BOD ranges and median values for leachates from 12 landfills are presented in figure 8. These are analyses of collection system samples only and were measurements done primarily by sewerage treatment plants which accepted the leachate for treatment. The COD ranges and median values for leachates from 12 sites are shown in figure 9. This data is less extensive since COD is commonly tested as a quarterly groundwater monitoring parameter by the landfill operator. Because the COD data was less extensive analyses of leachates from both collection systems and headwells have been pooled together. These BOD and COD concentrations are generally consistent with those reported in the literature for other MSW leachates.

From examination of this data two points are immediately evident: (1) the BOD and COD of these MSW leachates is very high and (2) there is a considerable amount of variability in these parameters between sites and even within a given site.

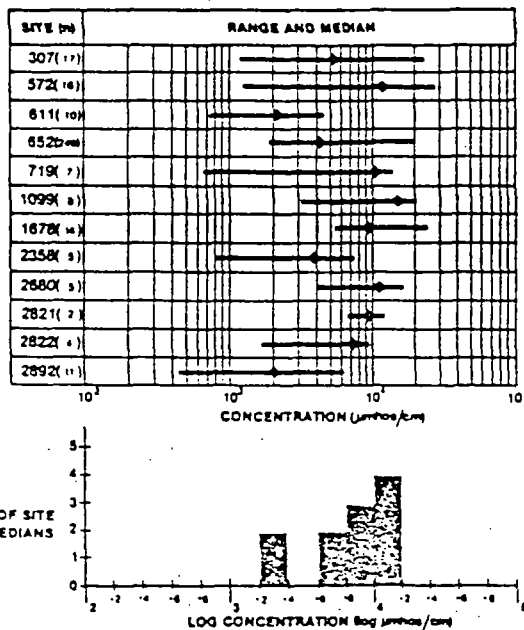


Figure 6 Site Ranges and Median Values for Specific Conductance

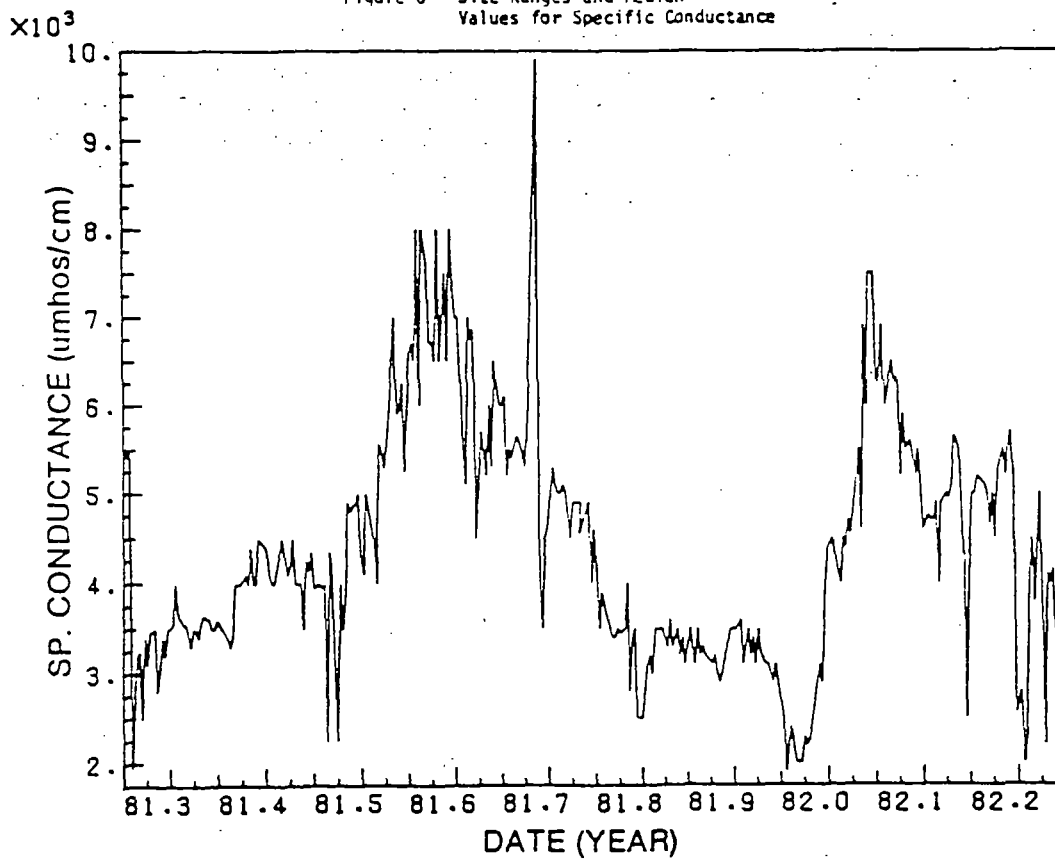


Figure 7 Leachate specific conductance over one year at Site 652

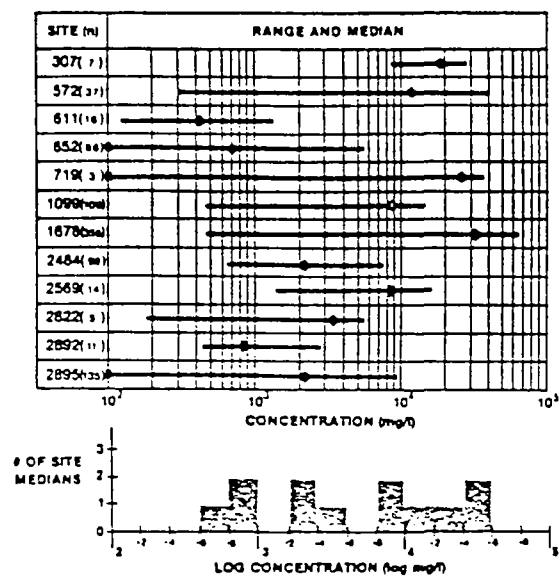


Figure 8 Site Ranges and Median Values for BOD

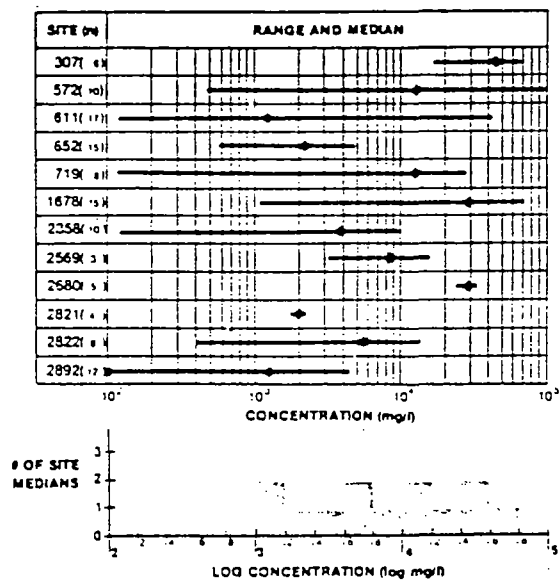


Figure 9 Site Ranges and Median Values for COD

The high organic strength of the leachates is of particular concern since this can result in a substantial organic loading on a treatment plant even though the daily quantity of leachate extracted may be relatively small (typically less than 10,000 gpd). The between site variability is difficult to account for but is probably a reflection of several design factors such as dilution by infiltrating groundwater (#652), dilution due to poor handling of surface water (#611), greater strength due to greater fill depth and codisposal of considerable quantities of high organic strength liquid industrial wastes (#1678).

The variability of the organic strength within a given site, while generally not as great as the concentration ranges might imply, can still be substantial. This variability can best be examined with plots of BOD values vs. time for select sites. This data is shown in figure 10 where test results for a year have been plotted for 2 sites. Each data point represents a grab sample for individual truckloads (#2895) or at a lift station (#652). From this figure it can be seen the leachate can vary considerably in organic strength even from truckload to truckload. For site #2895 there also appears to be a seasonally related strength variation with a peak occurring in the late summer and fall.

Nutrients (Nitrogen and Phosphorus)

Of the nutrients in MSW leachate, nitrogen and phosphorus are of major concern, principally because of their importance in biological treatment. A major contributor to nitrogen in MSW leachate is the decomposition of complex nitrogenous compounds in the garbage fraction of the waste. Within fill nitrogen cycling probably occurs as a result of continuous assimilation and release by the landfill's microbiological community. Thus, it is not surprising that the nitrogen in MSW leachate can be present in several organic and inorganic forms. In reporting the nitrogen content of leachate both the total kjeldahl nitrogen, which includes the organic and ammonia forms, and the oxidized anionic nitrates and nitrites must be considered.

The analysis of 11 MSW leachates for total kjeldahl nitrogen and ammonia nitrogen are depicted in figures 11 and 12. These figures show that both the total kjeldahl and ammonia nitrogen concentrations tend to fall in three groups of between 0-100 mg/l, 200-500 mg/l and one site (1678) at greater than 1000 mg/l. As noted previously, site 1678 is a codisposal site which accepts a large quantity of liquid industrial wastes for disposal and this could contribute to its high nitrogen content. Comparison of these figures and of individual analyses indicates that a majority of total kjeldahl nitrogen appears to be in the ammonia form. This is consistent with data reported in the literature for other MSW leachates.

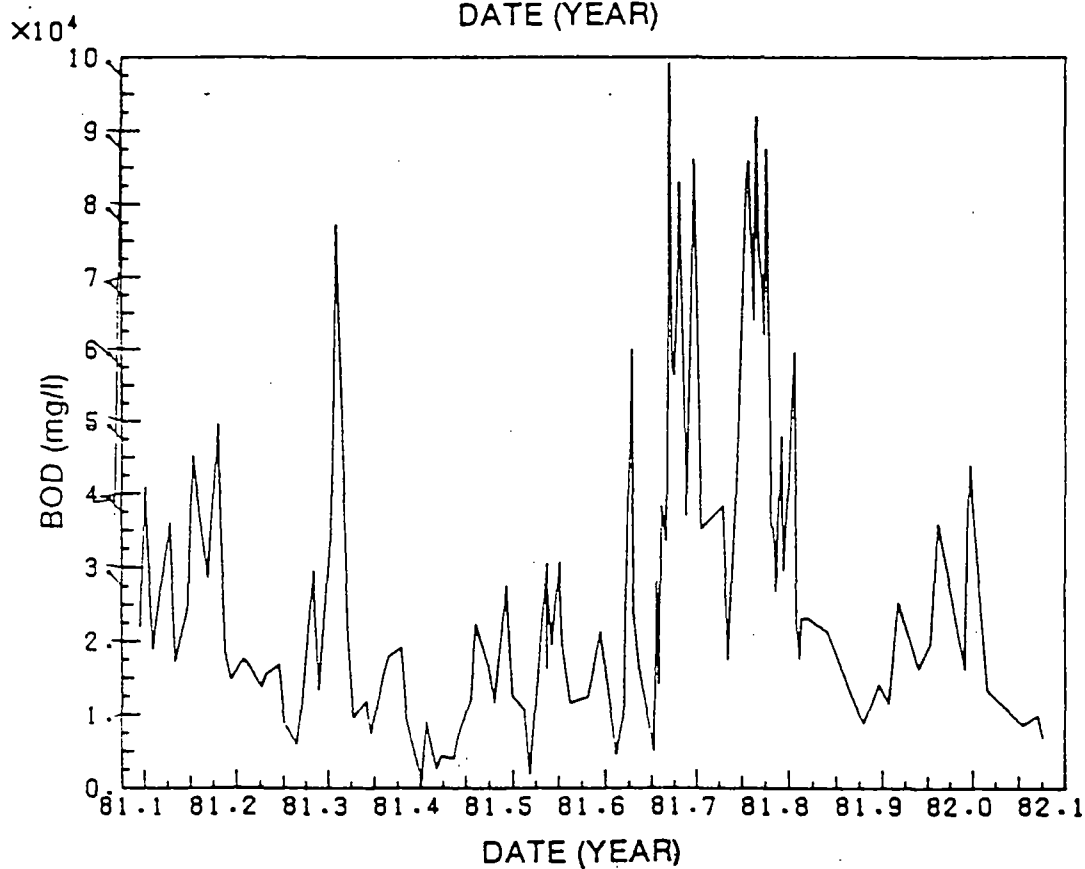
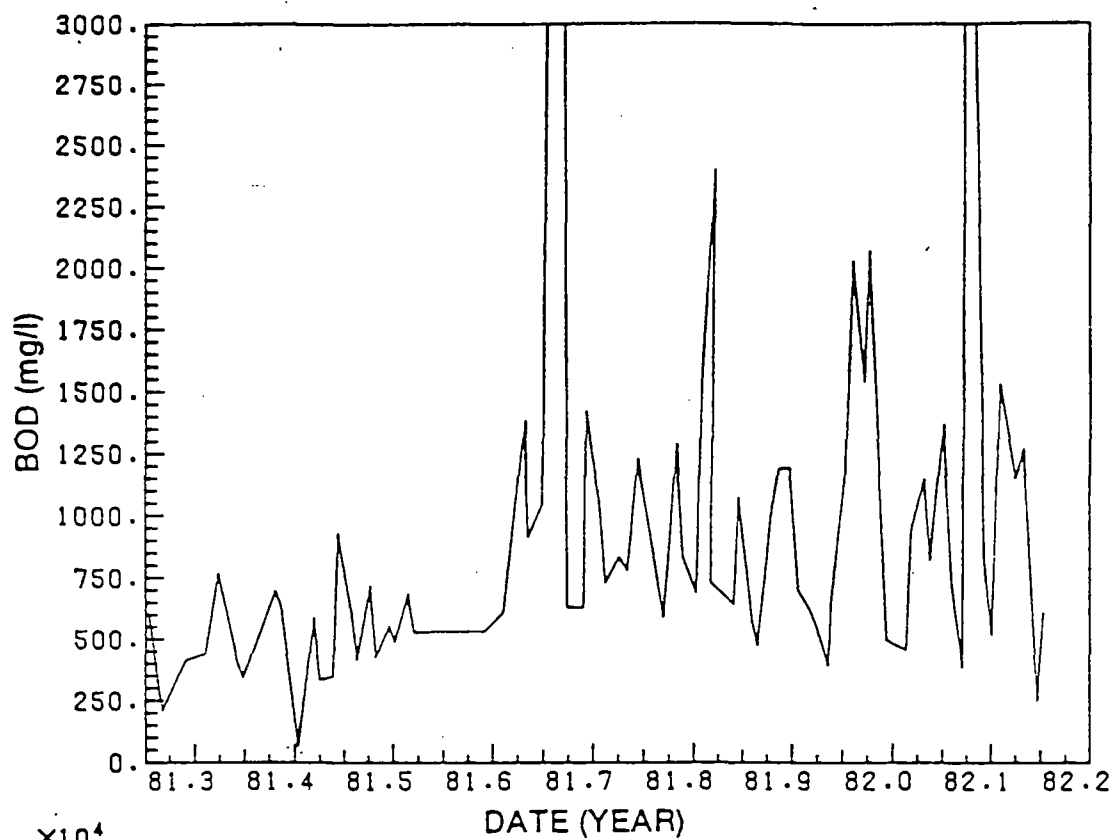


Figure 10 Leachate BOD over one year at Sites 652 (top) and 2895 (bottom)

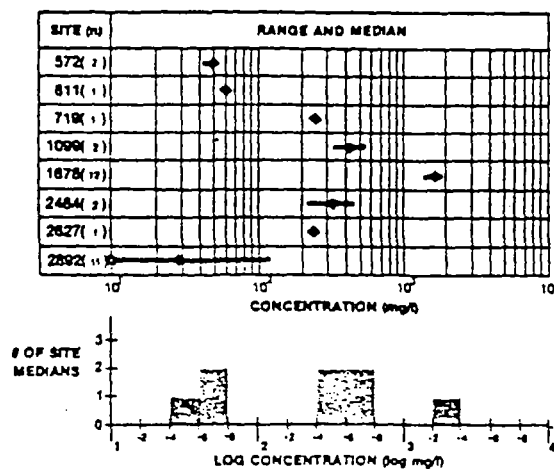


Figure 11 Site Ranges and Median Values for Total Kjeldahl-N

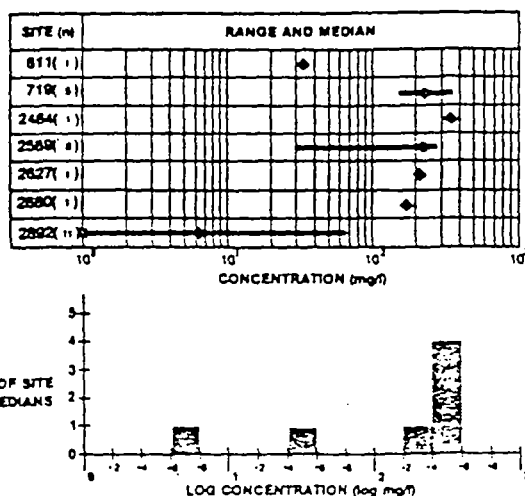


Figure 12 Site Ranges and Median Values for Ammonia-N

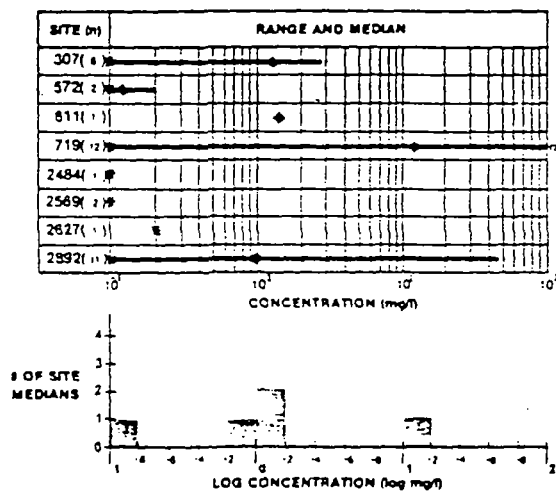


Figure 13 Site Ranges and Median Values for Nitrate-Nitrite-N

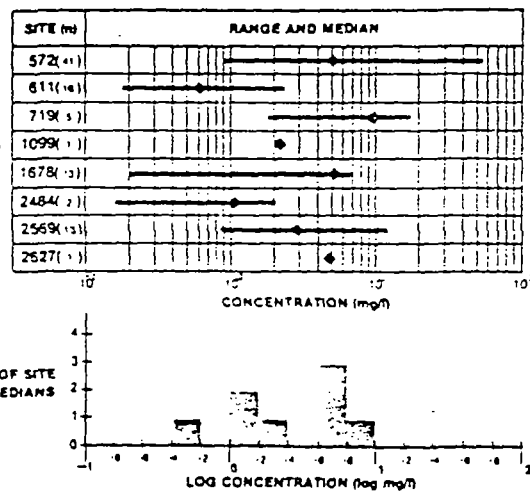


Figure 14 Site Ranges and Median Values for Total Phosphorus

Concentrations of nitrate and nitrite - nitrogen found in MSW leachates is shown in figure 13. Although the overall range is substantial the median values for all but one site were in the 0-2 mg/l range. These consistently low concentrations are not surprising when the reduced anaerobic nature of an MSW landfill is considered. The few high values that were reported are suspected of being a reflection of improper sample preservation and handling rather than true values.

Total phosphorus concentrations in the leachates of 6 sites is depicted in figure 14. In comparison to other parameters discussed so far these phosphorus concentrations are quite low. It is suspected this is a result of phosphorus being tied up within the fill due to absorption on cover soils and fixation due to reaction with metal complexes. This extremely low phosphorus level in MSW leachates is a characteristic commonly reported by several researchers. These low levels are of concern when considering leachate treatability as it is commonly estimated that to effectively treat an organic wastewater there must be a BOD to P ratio of 100 to 1. Most leachates have a ratio far in excess of this, indicating phosphorus addition is necessary unless the leachate is mixed with another wastewater stream with sufficient P content to compensate for this deficiency.

Hardness

Hardness, traditionally defined as a water's ability to precipitate soap, is a measure of the total quantity of polyvalent cations in a water sample. In natural waters hardness is principally a reflection of the presence of calcium and magnesium although in MSW leachate iron and possibly zinc may also be important.

The plot of the range and median total hardness values from ten MSW leachates in figure 15 shows that large ranges and some extremely high hardness concentrations were reported. Several sites reported hardness concentrations in excess of 10,000 mg/l with one sample as high as 225,000 mg/l. All site medians except one fell between 1,000-5,000 mg/l as CaCO_3 . These values include analysis of leachates from both headwells and collection systems. There is no readily apparent design or operational factor which appears to be causing some of the extremely high values. In general the hardness levels for these MSW leachates are consistent with those reported in the literature for other MSW leachates.

Alkalinity

As shown in figure 2 the pH variations at a given site are generally limited to a range of 1 to 1.5 pH units. This relatively low variability in pH can be attributed in part to these leachates' high buffering capacity. Total alkalinity is a

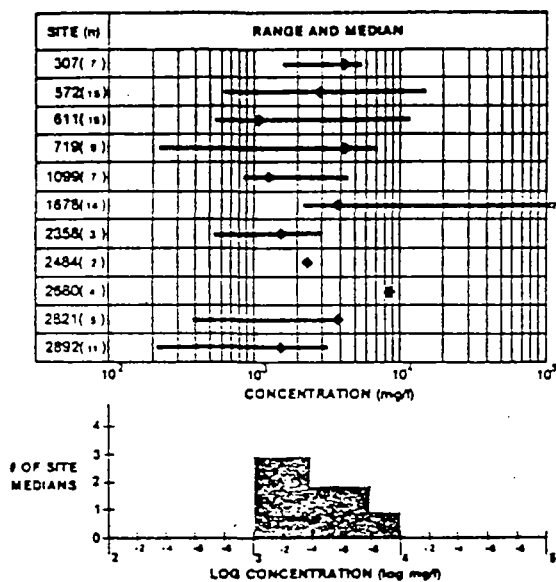


Figure 15 Site Ranges and Median Values for Hardness (CaCO_3)

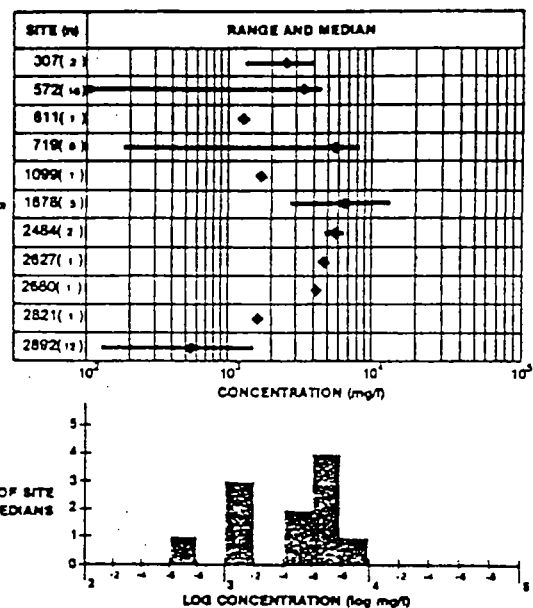


Figure 16 Site Ranges and Median Values for Alkalinity (CaCO_3)

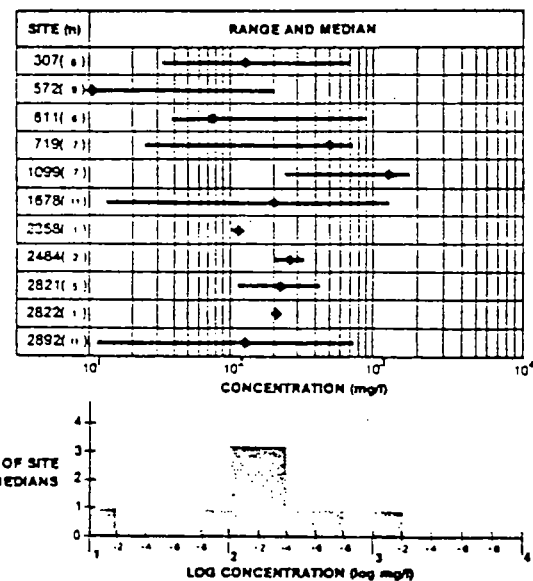
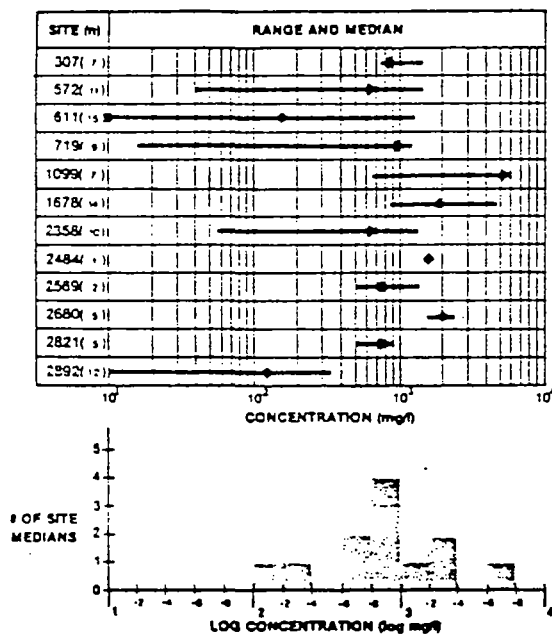


Figure 17 Site Ranges and Median Values for Chlorides(left) and Sulfates(right)

measure of this buffering capacity which for MSW leachates is probably derived from the presence of substantial concentrations of carbonate - bicarbonate, hydroxide and organically derived fatty carboxylic acids.

Analysis of the total alkalinity of leachates from 10 MSW landfills is shown in figure 16. Included are analyses of samples from both collection systems and head wells. The data is somewhat limited in that several sites reported only 1 analysis. The overall range of values reported was substantial at 4-10,600 mg/l although individual site concentrations often span a considerably smaller range within these limits. Most values and site medians were clustered between 1,000 and 10,000 mg/l.

Chlorides & Sulfates

Several researchers have shown the principle inorganic anions in MSW leachate are chlorides and sulfates. The predominance of these anions in MSW leachate is a reflection of their presence in many of the wastes disposed of and their high solubility. Chloride is particularly reflective of a landfill's leaching behavior due to its chemical stability, remaining as a free ion under a wide range of redox conditions. Sulfate leaching probably follows a more complex route than chlorides. The strong reducing conditions within an MSW landfill probably causes a reduction of some sulfate to sulfide, which is a powerful precipitant with many metals. In addition to metal precipitation, sulfur can be assimilated biologically so there is probably some biocycling of this element as leachate passes through the fill.

The ranges and median values for chloride and sulfate analyses of several MSW leachates are shown in figure 17. Included are analyses from both collection system and head well samples. With the exception of two sites, chloride concentrations were generally less than 2,500 mg/l with median values clustering between 600-2,500 mg/l. Sulfate concentrations had a somewhat smaller overall range with medians clustered mainly between 70-500 mg/l.

Iron

Iron is a common metal in MSW leachate, with the reddish-brown color of many MSW leachates usually attributed to its presence. The individual site ranges and median values of iron concentrations reported for 12 MSW leachates are shown in figure 18. As can be seen in this figure, the overall range of concentrations measured was substantial as were the ranges at individual sites. Median values were generally well distributed throughout this range although there was a clustering of several sites at 10-30 mg/l.

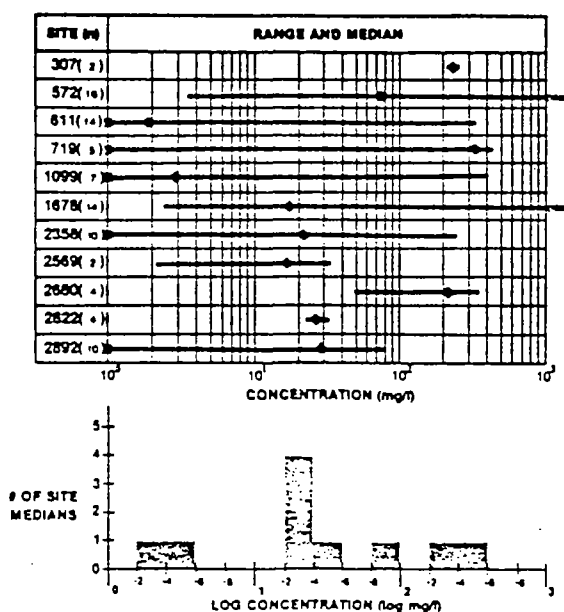


Figure 1d Site Ranges and Median Values for Iron

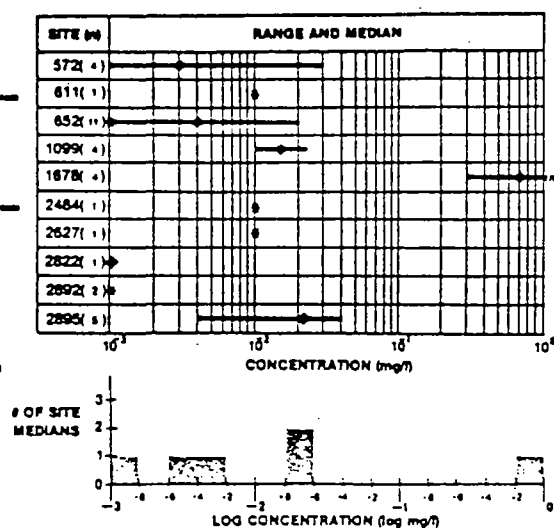


Figure 19 Site Ranges and Median Values for Arsenic

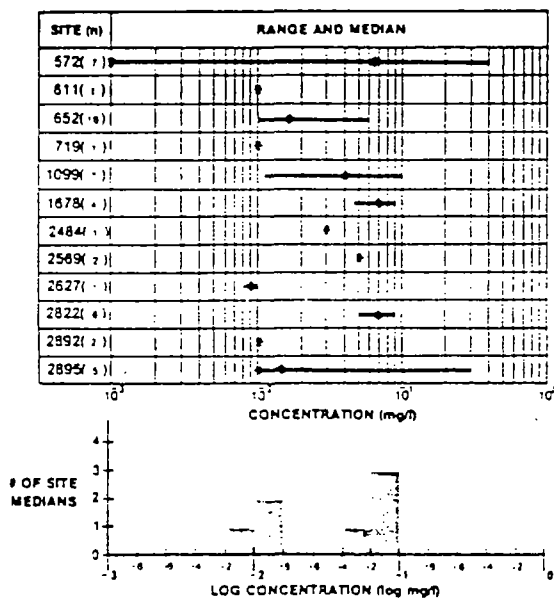


Figure 20 Site Ranges and Median Values for Cadmium

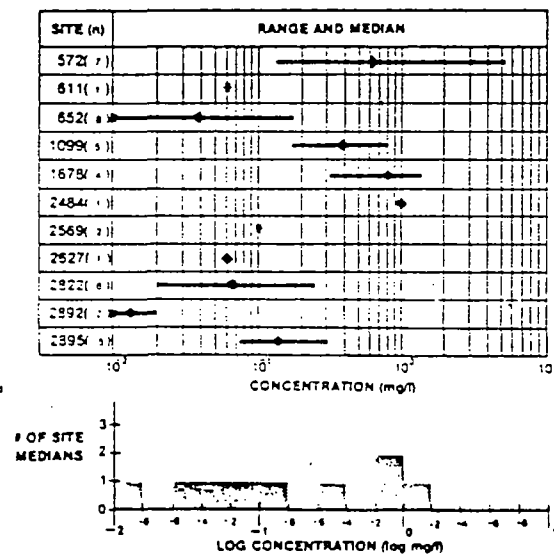


Figure 21 Site Ranges and Median Values for Chromium

This wide range of iron concentrations is consistent with that reported in the literature. The considerable range encountered is thought to be a reflection of the sensitive nature of iron's chemistry. Due to the acidic, reduced state of fresh leachate iron is probably present in the soluble ferrous state. However, upon retrieval if a leachate sample is exposed to the air the ferrous ions can be rapidly oxidized to a low solubility ferric state. If filtered after this oxidation has occurred, precipitated iron will be removed from the sample and not reflected in the analysis. In contrast, if the leachate is not filtered prior to acid preservation, natural soil particles retrieved with the leachate may contribute to its iron content. These two factors alone can result in considerable swings in a given site's leachate iron concentration.

Other Metals and Inorganics

In addition to the previously discussed parameters, MSW leachate is known to contain a wide variety of trace metals and other inorganic contaminants. MSW leachate from several Wisconsin sites have been analyzed for many of these contaminants. The results of most of these analyses are presented in table 2. Where sufficient data was available, the site ranges and median values have also been presented in figures 19-31.

This data confirms that analyses in the literature that sodium and potassium, followed by zinc and manganese are major inorganic cations in MSW leachates. Aluminum may also be present at substantial concentrations although its presence at high levels is sporadic. Boron was next in concentration, although with only two analyses reported, its presence at these levels needs confirmation. The remaining contaminants, with the exception of occasional values, were generally present in concentrations of less than 1 mg/l. This does not lessen their importance, however, since many of these contaminants are very toxic.

These results are generally comparable to those reported in the literature for other MSW leachates, where such data was available for comparison.

As with many of the other parameters previously discussed, the codisposal of substantial quantities of industrial and hazardous waste at sites 1678, 1099 and 572 appears to have significantly altered the leachate characteristics at these sites. Of particular note are the following parameters which had readily apparent higher concentrations at these codisposal sites (the sites are identified in parentheses): arsenic (1678), chromium (572), copper (1099), cyanide (572 & 1678), lead (1099 & 1678), nickel (572 & 1678) and zinc (572, 1099 & 1678). The fact that site 1678 was more consistently higher than the other two codisposal sites probably reflects the larger quantity and wider variety of industrial and hazardous wastes disposed of at this site.

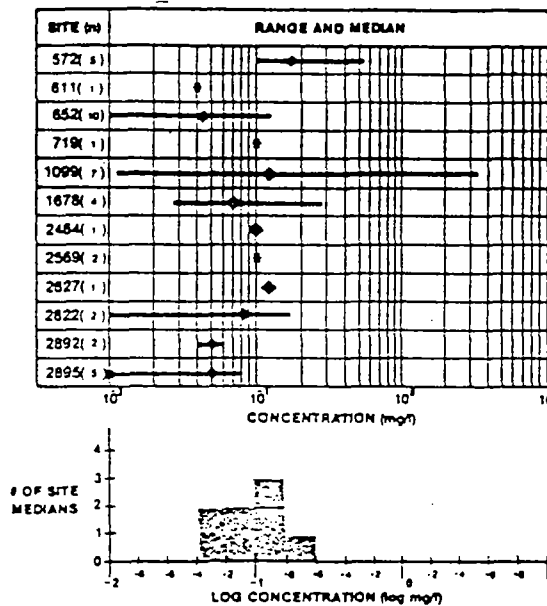


Figure 22 Site Ranges and Median Values for Copper

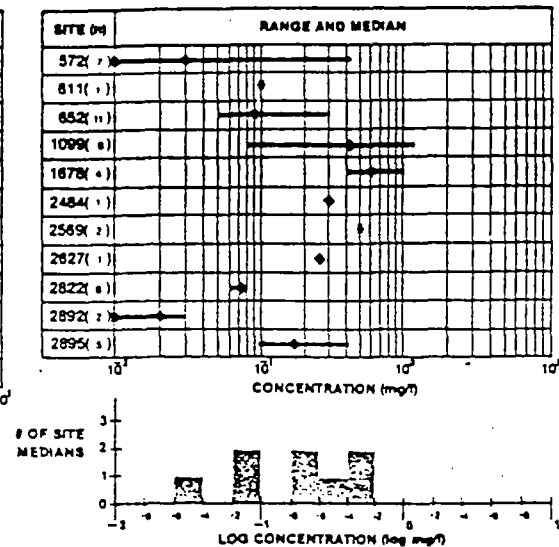


Figure 23 Site Ranges and Median Values for Lead

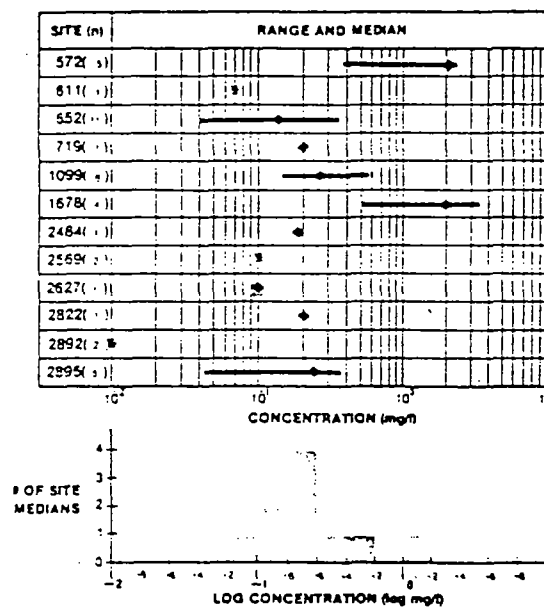


Figure 24 Site Ranges and Median Values for Nickel

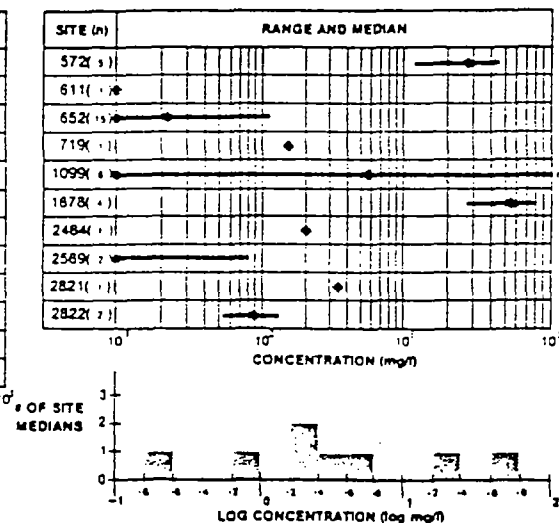


Figure 25 Site Ranges and Median Values for Zinc

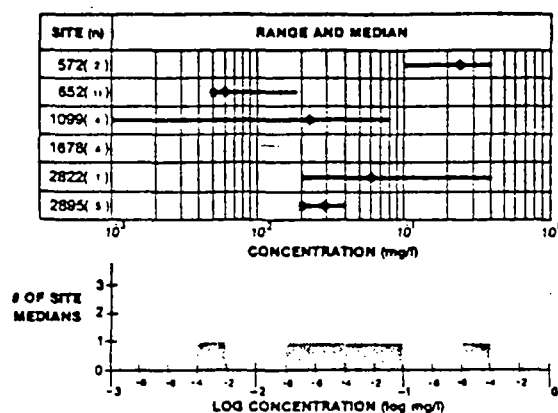


Figure 26 Site Ranges and Median Values for Cyanide

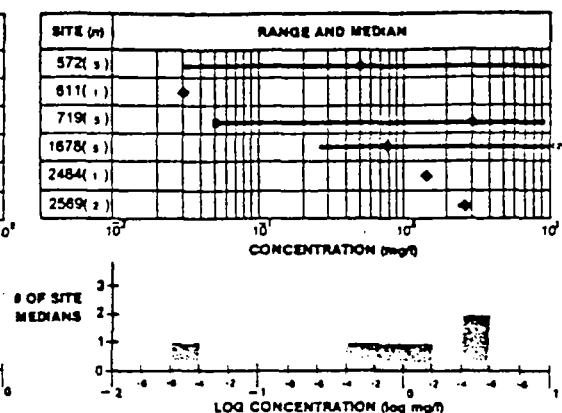


Figure 27 Site Ranges and Median Values for Manganese

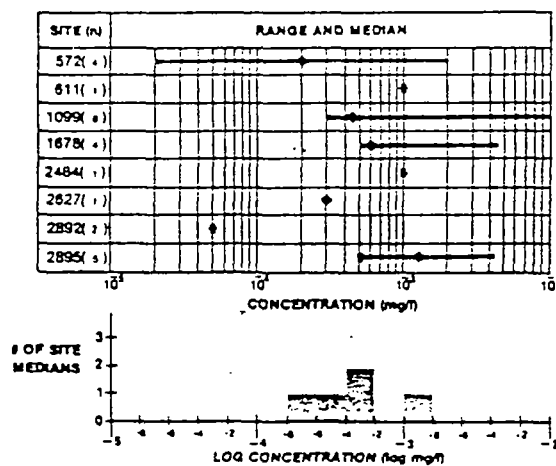


Figure 28 Site Ranges and Median Values for Mercury

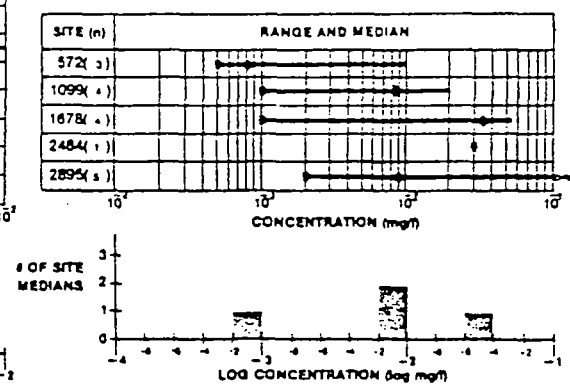


Figure 29 Site Ranges and Median Values for Silver

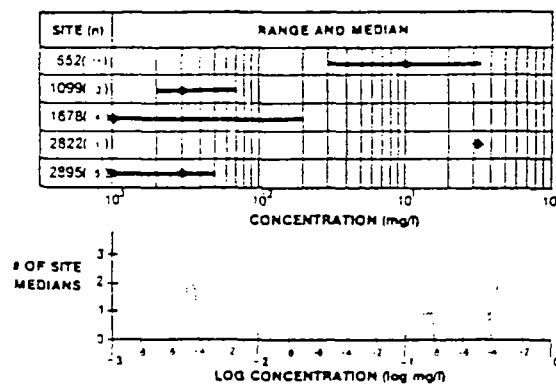


Figure 30 Site Ranges and Median Values for Thallium

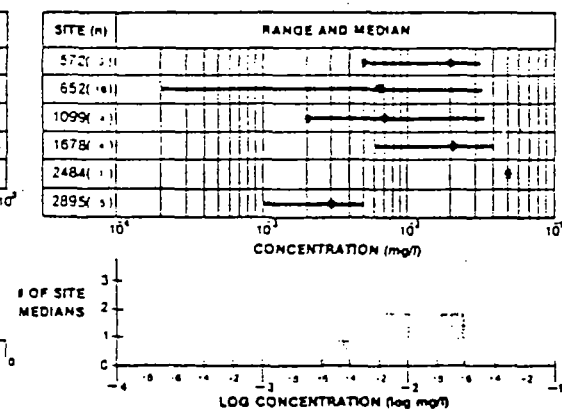


Figure 31 Site Ranges and Median Values for Selenium

Trace Organics

MSW leachate contains considerable concentrations of organic compounds as reflected by its high BOD and COD. These parameters can provide an overall indication of the presence of organics but fail to identify specific compounds. Analysis of MSW leachates by several researchers has identified many organic compounds which are apparently by-products of the natural decomposition of waste. These include organic acids, phenolic compounds and longer chain organics such as lignins. Because of the wide variety of organic chemicals utilized in manufacturing processes and products one would expect to also find numerous synthetic organic compounds in MSW leachate. These man-made organics, generally found in very small quantities, are of concern because of their possible toxic, carcinogenic or mutagenic properties coupled with their persistence in the environment.

MSW leachate samples from 5 Wisconsin landfills have been analyzed for the 114 organic compounds which the U.S. EPA has proposed to designate as priority pollutants. MSW leachates from another 3 sites have been analyzed for a less extensive list of organics. Table 3 lists those organic compounds that were detected in these leachates and presents the overall range and median values where sufficient data exists. This table shows that 36 of the 114 priority pollutant organics were detected in these leachates.

The 114 priority pollutant organics have been divided into five classes which reflect the nature of the compounds on the basis of separation methodology. Division of the 36 identified organics in these leachates were: 3 of a possible 11 organic acids, 23 of 32 volatile organics, 8 of 46 base-neutral organics, 1 of 19 chlorinated pesticides and 1 of 7 PCB isomers. It should be noted that many of these compounds were detected in only one of the leachates tested and then only at extremely low levels so their actual presence is questionable. There were, however, 10 compounds which were detected in at least one-half of the leachate samples analyzed: phenol; methylene chloride; toluene; 1, 1 dichloroethane; trans 1, 2 dichloroethane; ethyl benzene; chloroform; bis (2 ethyl hexyl) phthalate; diethyl phthalate and dibutyl phthalate. Also of note are 3 compounds which do not fall into the above group but were detected at significant levels in at least one leachate: 1, 2 dichloroethane; 1, 1, 1 trichloroethane and isophrone.

Considering the nature of their uses it is not surprising that some of these compounds were detected in all the leachates analyzed. Methylene chloride, for example, is widely used in the manufacture of paint and varnish removers, insecticides, solvents and pressurized spray products. Phthalates are also widely used, primarily as plasticizers in the manufacture of various plastics. Another common industrial compound, toluene, was also detected in all five leachates analyzed.

A more detailed comparison of the organic compounds detected at codisposal sites with other MSW landfills did not reveal any apparent increase in the number of organic compounds detected, although some concentrations were higher in some codisposal sites. No data on other MSW leachates was available with which to compare these analyses. The lack of data on these compounds in MSW leachate and their environmental significance indicates the need for additional work in this area.

Comparison to Municipal Wastewater Quality & Inhibitory Levels

A summary of the contaminant concentrations in the MSW leachates discussed in this report is presented in table 4 along with values reported in the literature for a "typical" municipal wastewater. Also included in this table are levels at which these contaminants are reported to inhibit various types of biological treatment processes.

An examination of this table shows that Wisconsin MSW leachates tested were substantially higher than typical municipal wastewater for a majority of the parameters reported, reflecting its highly contaminated nature. These high levels raise a concern that biological treatment processes could be upset by several contaminants in MSW leachate. One method to address this concern is to compare leachate contaminant concentrations with inhibitory levels reported in the literature for these contaminants. Table 4 presents such a comparison. Although interactions between parameters are not considered, it does provide a rough indication of which contaminants are of the greatest concern. This comparison reveals that the maximum limit of the range encountered for the raw leachate did, in fact, exceed the inhibitory levels for a number of parameters. When a comparison is made using a "typical" range as the expected concentration of contaminants in MSW leachate, however the number of parameters exceeding inhibitory levels drops considerably with only nickel and zinc likely to interfere with aerobic treatment processes and cadmium, iron and zinc likely to interfere with an anaerobic digestion process.

All MSW leachates currently generated in Wisconsin are being treated at existing municipal wastewater treatment plants (Table 1). Since the leachate is mixed with the plant influent and is a small percentage of the total flow the resultant dilution of the leachate contaminants should make exceedance of any inhibitory levels rare. However, close monitoring of leachate chemical characteristics to insure against treatment plant upset is desirable, especially considering the variability in these characteristics at many sites.

Perhaps a more important factor in biological treatability of MSW leachate is its extremely high organic strength as expressed by its BOD and COD. Raw leachate is nutrient poor, especially in total P, and effective treatment of this organic strength could

Table 4: Comparison of MSW Leachate Contaminant Concentrations to Municipal Wastewater Quality and Inhibitory Levels for Biological Treatment

Parameter	MSW LEACHATE (Wisconsin Data)		"Typical" (1) Concentration In Municipal Wastewater (mg/l)	INHIBITORY CONCENTRATION (2)		
	Range (mg/l)	Typical (mg/l)		Activated Sludge (mg/l)	Anaerobic Digestion (mg/l)	Nitrification (mg/l)
T. Alkalinity	4-10630	500-10000	280 (bicarb only)			
Aluminum	ND-85.0		0.01-0.03	15-26		
Arsenic	ND-70.2	ND-0.4		0.1	1.6	
BOD ₅	67-64500	400-40000	200			
Boron	4.6-5.1			0.05-100	2	
Cadmium	ND-0.40	ND-0.10	0.002-0.009	10-100	0.02	
Calcium	200-2100			10-100		
Chloride	2-5590	100-2500	20-100	2500		
T. Chromium	ND-5.60	ND-1.0	0.1-0.15	8000-15000		
COO	62-97900	500-50000	400	50	50-500	
Copper	ND-3.56	ND-0.5	0.02-0.1	1.0	1.0-10	0.005-0.5
Cyanide	ND-0.40	ND-0.40		0.1-5	4	0.34
Iron	0.06-1500	ND-500	0.12-0.2	1000	5	
Lead	ND-1.2	ND-1.2	0.05-0.1	0.1		0.5
Magnesium	120-780		10-40		1000	50
Manganese	ND-20.5	ND-10	0.02-0.03	10		
Mercury	ND-0.01	ND-0.005	0.00005-0.00015	0.1-5.0	1365	
Ammonia-N	ND-359	0-350	25-60	480-1600	1500	
NO ₂ -N	ND-250	0-10	0-1.0			
Nickel	ND-3.3	ND-3.3	0.075-0.170	1.0-2.6		0.25
Phenol	0.48-112	2-20		200		4-10
T. Phosphorous	0.16-53	0-10	5-35			
pH	5.8-7.66	5.8-7.6	6-8.5			
Potassium	31-560		7-15			
Silver	ND-0.196	ND-0.05		5		
Sodium	33-1240		23-80		3500	
TDS (3)	480-24000	1000-20000	250-850	16000		
TSS	5-18800	100-1000	200			
Sulfate	ND-1800	50-1500	15-80			500
Zinc	ND-162	ND-75	0.04-0.1	0.08-10	5-20	0.08-0.5

(1) WPCF, ASCE (1977); Klei et al (1980)

(2) WPCF, ASCE (1977); Eckenfelder & Ford (1970); USEPA (1977)

(3) Assumed (TDS = 1.0 x conductivity) for this analysis

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Table 5: Comparison of MSW Leachate Contaminant Concentrations to Drinking Water Standards

Parameter	Drinking Water ¹ Standard (mg/l)	# of Samples Exceeding Standard	# of Site Medians Exceeding Standard
Arsenic	0.05	4 of 33 (12%)	1 of 10 (10%)
Barium	1.0	1 of 9 (11%)	1 of 5 (20%)
Cadmium	0.01	39 of 52 (75%)	6 of 12 (50%)
Chromium	0.05	31 of 44 (70%)	7 of 11 (64%)
Lead	0.05	33 of 45 (73%)	7 of 9 (78%)
Mercury	0.002	4 of 27 (15%)	0 of 8 (0%)
Nitrate (as N)	10.0	7 of 27 (26%)	1 of 3 (33%)
Selenium	0.01	9 of 33 (27%)	2 of 6 (33%)
Silver	0.05	2 of 28 (7%)	0 of 5 (0%)
(Secondary)			
Chloride	250	80 of 108 (74%)	8 of 12 (67%)
Copper	1.0	1 of 40 (2.5%)	0 of 12 (0%)
Iron	0.3	79 of 83 (95%)	12 of 12 (100%)
Manganese	0.05	6 of 10 (60%)	5 of 6 (83%)
pH	6.5 - 8.5	245 of 432 (57%) ³	4 of 12 (33%) ³
Sulfate	250	26 of 66 (39%)	4 of 11 (36%)
TDS ²	500	347 of 348 (100%)	12 of 12 (100%)
Zinc	5.0	12 of 44 (27%)	3 of 10 (30%)

¹40 CFR Parts 141 and 143²Assumed (TDS = 1.0 x conductivity) for this analysis³All exceedances below standard

26585

not be achieved without nutrient addition. This high organic strength could also easily upset an existing municipal wastewater treatment plant unless precautions are taken to minimize organic load variation during discharge of leachate to the plant influent.

Comparison to Drinking Water Standards

A useful benchmark in obtaining a perspective on the contaminant concentrations in landfill leachate are drinking water standards (dws). The U.S. EPA has established standards based on health considerations ("primary" dws) and on aesthetic considerations ("secondary" dws). Those standards for which data on MSW leachate was available are listed in Table 5 along with an indication of the number of leachate samples and site medians exceeding each standard.

As can be seen from this table, all primary and secondary dws were exceeded, although the percent of samples exceeding the standard varied widely from parameter to parameter. Those contaminant limits that were exceeded in at least 50% of the samples analyzed were:

Primary dws - cadmium, chromium, lead

Secondary dws - Chloride, iron, manganese, pH and TDS

In general, these exceedances were well in excess of the 50% level. Of particular note are iron and TDS which exceeded the standard in over 90% of the MSW leachate samples tested.

Although a comparison of individual samples to these standards is revealing, the analysis can be overly influenced by one site's data. This problem can be avoided by comparing site medians with the standard as is done in the third column of table 5. This comparison reveals essentially the same pattern with the exception that selenium has been elevated to the 50% level and pH has dropped below the 50% level.

This analysis is also useful in evaluating the degree of protection provided by groundwater standards for MSW landfills based on drinking water standards. The U.S. EPA currently defines unacceptable groundwater contamination by a landfill as causing exceedances of primary dws at the waste boundary. At the time of the writing of this paper (June, 1982) a similar standard is being considered in Wisconsin.

The lack of consistent exceedances of primary dws in the leachate itself raises a question as to whether a sufficient degree of groundwater protection is provided by such a standard, especially considering the lack of mobility of many of these contaminants in soils and groundwater. An analysis similar to one presented here, along with consideration of other factors,

has potential for use to determine the appropriateness of utilizing drinking water standards as performance criteria for municipal solid waste landfills.

Summary

This report has summarized data on the chemical characteristics of leachate from 16 municipal solid waste landfills in Wisconsin. The data was compiled from Department of Natural Resources files and represents analyses done primarily by site operators and wastewater treatment plants. Only analyses of samples from leachate collection systems and headwells have been included.

A summary of reported concentrations for the wide variety of contaminants in these leachates is provided in table 2. The overall ranges determined were generally similar to that reported in the literature for other MSW leachate, although some of the extremes were not experienced. Where sufficient data was available a narrower range within which most values fell has been presented to provide a better indication of the likely composition of MSW leachate for design purposes. Care should be taken in using this summary, however, since considerable variability both between sites and within a given site was experienced.

In general, these leachates were slightly acidic with very high organic and dissolved solids concentrations. Lesser but still substantial quantities of total kjeldahl nitrogen, hardness, alkalinity, chlorides and sulfate were also present. Iron was the major metal present in these leachates followed by zinc and manganese. Also present were a wide variety of other organic and inorganic contaminants, mostly at levels less than 1 mg/l. This includes several priority pollutants, both metals and trace organics.

Codisposal of substantial quantities of industrial wastes, both hazardous and nonhazardous appears to have increased the concentration of many contaminants in the leachates from these sites when compared to other MSW landfill leachates in Wisconsin.

Most of the contaminants in these leachates were well in excess of what one would expect to find in a typical municipal wastewater. With the exception of occasional high values these levels do not appear to be high enough to inhibit biological treatment, especially if the leachates are discharged to an existing wastewater treatment plant at a low percentage of the total influent flow. Close monitoring of leachate characteristics is still desirable, however, as some parameters do, on occasion, exceed inhibitory levels. Of greater concern appears to be the potential for treatment plant upset brought on by the high organic strength of these leachates. This should be avoidable through careful control of flow.

Exceedance of all primary and secondary drinking water standards did occur although the frequency at which this occurred varied considerably from parameter to parameter. Of those exceeded, iron and TDS are the most consistent with nearly all leachate samples and all site medians exceeding established standards.

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Aquifer contamination and protection

Project 8.3 of the
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II-6 Trace-element pollution of ground waters in industrial-urban areas in Poland

by

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II-6.1 INTRODUCTION

The pollution of the natural environment changes the trace-element composition underground. The trace elements derived from pollutants move into ground waters, directly from waste-disposal reservoirs and sewage systems from which leakage occurs. They also can be washed out by the rain waters infiltrating the soil zone, from solid waste materials deposited on the surface of the earth and pollutants distributed into the atmosphere. Some trace elements are essential for life, others toxic or cause disease from excess.

The knowledge of the trace-element, environmental-background level and the changes occurring is essential to biologists and also to hydrogeologists when the concentrations exceed the maximum permissible levels in ground waters. The data collected on trace element occurrences in ground water may also enable the identification of pollutant sources derived from urban-industrial or agricultural impact and can be useful in tracing the pollution movement into ground waters.

Gross survey of trace elements in pollutant sources and in ground waters (polluted and unpolluted) has been carried out with the purpose of obtaining a picture of the present state of water pollution particularly in urban and industrial areas.

The purpose of this case study is to show the correlation between water quality and trace element occurrences underground in urban and industrial areas and the pattern of pollutant movement. The investigations are restricted mainly to Quaternary sand aquifers. The data have been collected during the years 1974-1976 from the central region of Poland.

II-6.2 EXPERIMENTAL METHODS

X-ray fluorescence and reactor neutron activation have been used to identify the elemental components in ground waters and industrial effluents. These techniques offering very good minimum detection limits and have the ability to determine simultaneously more than 20 elements.

The samples representing the sources of pollutants have been taken from industrial and municipal sewage systems, industrial waste storage reservoirs and effluents released from several industrial plants including; chemical, textile, pharmaceutical, sugar, food, rubber, leather, cellulose, soda, metallurgical and alcohol distillation plants. The rivers were sampled downstream from the industrial and municipal sewage outlets at a distance ensuring mixing of the river water. The samples representing unpolluted ground waters have been collected from deep Cretaceous and Tertiary aquifers (Tritium content below 5 TU) and from Quaternary waters of areas free of contamination. The sampling depth extended from 5 to 40 meters.

The polluted waters have been selected according to the results of the chemical analysis reflecting the changes of water quality. About 120 wells have been sampled in industrial and urban areas with populations of about 30,000 to 60,000. The sampling depth extended from 10 meters to 40 meters in partially-confined sand aquifers. Analytical results for 18 trace elements are summarized in Table II-6.1.

The range and average concentrations in the unpolluted waters represent the natural environmental level which can be used as a background in estimating the trace-element pollution underground. The analytical data obtained for industrial and urban areas shows a much broader range of concentrations and higher average values. For several elements, such as zinc, selenium, cobalt and barium the observed concentrations are from ten to one hundred times higher than in unpolluted waters. The movement of trace-element pollutants with ground water can be observed on the frequency distribution diagram shown in Figure II-6.1, constructed for Zn, Co, Cr, Sb, Se, Yb. The dashed lines divide the distributions in regions of naturally occurring trace elements (A) and pollutants (B).

The data obtained for rivers and industrial effluents show with respect to unpolluted waters very high concentration levels (Table II-6.1). Visual imprint of the composition and concentration levels can be obtained in a diagram shown in Figure II-6.2. It can be noted that the concentrations in polluted waters are up to a thousand times higher than in unpolluted waters.

II-6.3 GROUND-WATER QUALITY AND TRACE ELEMENT OCCURRENCE

The ground-water quality is usually reflected in its physical and chemical indicators. Knowing that trace element concentrations in ground waters partly originate from pollution one should search for correlation between physical and chemical indicators and trace element occurrence.

An investigation was carried out on an urban-industrial area. The wells were simultaneously sampled for chemical and trace element analysis. Cross section of the investigated area and analytical results are presented in Figure II-6.3. A good agreement between chemical and trace element data may be noticed, however the appearance of single indicators is selective and one may observe several differences, which would require additional detailed examination. It can be also noted, that the high concentrations of trace elements reflect the industrial impact. This can not be always stated regarding chemical indicators. It can be seen in well No. 33, with a very high concentration of chromium, which probably has originated at the metallurgical plant in this area (see also II-8).

II-6.4 PATTERNS OF CONTAMINANT MOVEMENT

II-6.4.1 Leakage from reservoirs

Direct contaminant input to aquifers can be caused by leakage from waste-disposal reservoirs and sewage channels from which large volumes of polluted water may infiltrate into the aquifer. This can be observed in the data obtained from two following case studies (Figure II-6.4).

The water seepage through an earth filled dam is contaminating adjacent ground waters. The concentration diagram presents a relative decrease of trace-element concentrations with the distance from the dam (Figure II-6.4A).

In Figure II-6.4B the polluted waters from a metallurgical-waste reservoir have leaked directly to well No. 5 at a distance of 1000 metres. The diagram indicates dilution of polluted waters by the ground water. The concentration plots are similar to those presented previously but because of different composition of waters they are more evident. Strontium, rubidium and cobalt dominate in the reservoir water, zinc and

TABLE II-6.1 Concentration of trace elements in ground waters, rivers and in industrial effluents

Element	Concentration (ug/litre)									
	Groundwaters						Rivers		Industrial Effluents	
	Natural Environment			Urban-Industrial Areas			No. of Samples	Range	No. of Samples	Range
	No. of sampled wells	Range	Average	No. of sampled wells	Range	Average				
Scandium	38	0.01 - 0.35	0.07	77	0.01 - 2.18	0.10	18	0.005- 0.165	19	0.002- 0.47
Chromium	42	0.07 - 2.00	1.0	98	0.2 - 15.2	3.0	17	0.5 - 22.9	24	1.1 - 520
Cobalt	42	0.01 - 0.13	0.03	125	0.01 - 7.9	0.6	19	0.03 - 0.71	23	0.02- 32.2
Zinc	26	1.5 - 80	15	111	1.5 - 6840	310	30	3.0 - 57	24	7.0 - 2200
Selenium	38	0.01 - 0.08	0.05	88	0.05 - 7.5	0.48			16	0.07 - 4.4
Bromine	26	12 - 150	30	66	24 - 5290	530	28	86 - 2130	16	0.001-2200
Ruthenium				45	0.002 - 0.5	0.03				
Rubidium	18	0.05 - 2.5	1.5	26	0.03 - 13.8	2.4	19	0.4 - 5.5		
Strontium	26	10 - 1240	100	95	11 - 5070	290	15	0.9 - 394	21	13.7 - 6700
Antimony	26	0.13 - 1.0	0.3	67	0.1 - 4.5	1.0	20	0.11- 1.4	22	0.13- 36.8
Caesium	28	0.003- 0.027	0.01	83	0.003- 0.5	0.03	16	0.001- 0.26	19	0.02- 33.1
Barium	28	3 - 60	15	48	3 - 913	85	8	10.5 - 49.3	12	3 - 54.3
Lanthanum	24	0.02 - 0.47	0.12	57	0.07 - 19.7	3.5	12	1.3 - 9.5		
Cerium	32	0.04 - 3.2	1.0	74	0.1 - 11.0	2.7	32	0.7 - 2.5	8	0.07- 8.0
Ytterbium	34	0.001- 0.2	0.04	103	0.001- 0.6	0.11	16	0.01- 0.41	6	0.001-1.6
Hafnium	16	0.003- 0.4	0.12	42	0.003- 0.9	0.04				

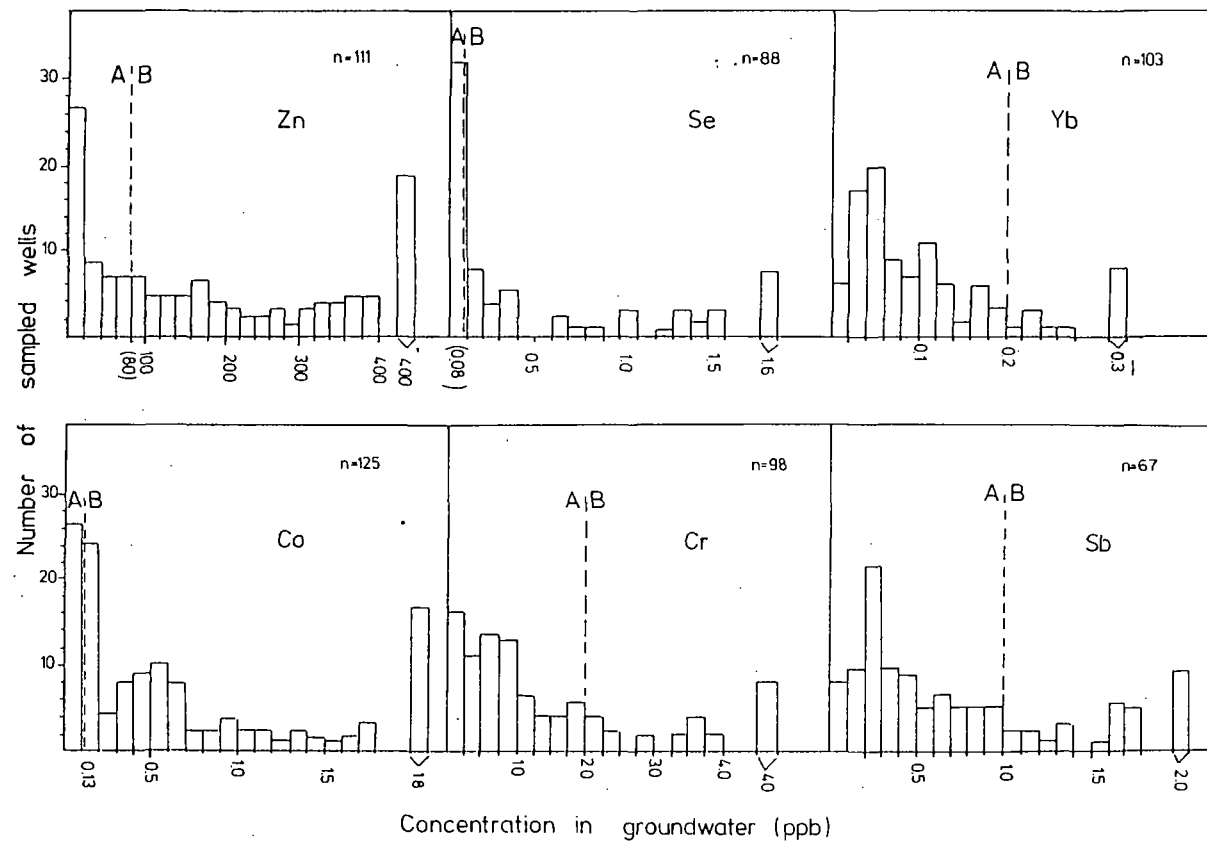


Figure II - 6.1 The frequency distribution of Zn, Co, Cr, Sb, Se, Yb in ground water, sampled in urban-industrial areas. Dashed line indicates the maximum concentration observed in unpolluted water. Range "A" corresponds to natural occurring concentrations. Range "B" results from movement of pollutants to ground water.

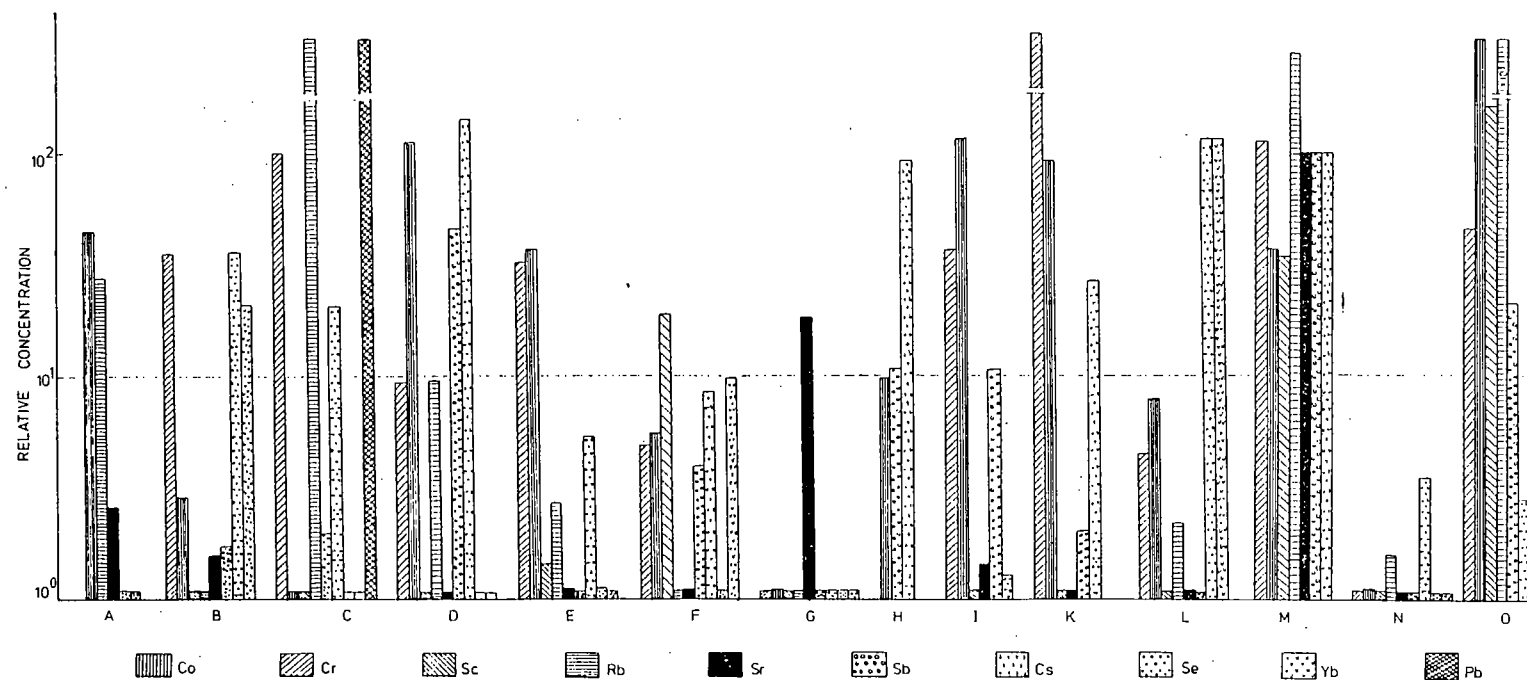


Figure II - 6.2 Trace elements deriving from industrial effluents. The concentrations are shown with respect to unpolluted ground water.
 A - Phosphate plants, B - Metallurgical plants, C - Lead Processing D - Flotation plants, E - Chemical factories, F - Pharmaceutical factory, G - Rubber production, H - Dyes factory, I - Textile plants, K - Lether tannery, L - Cellulose plants, M - Soda plants, N - Food plants, O - Alcohol distillation plants.

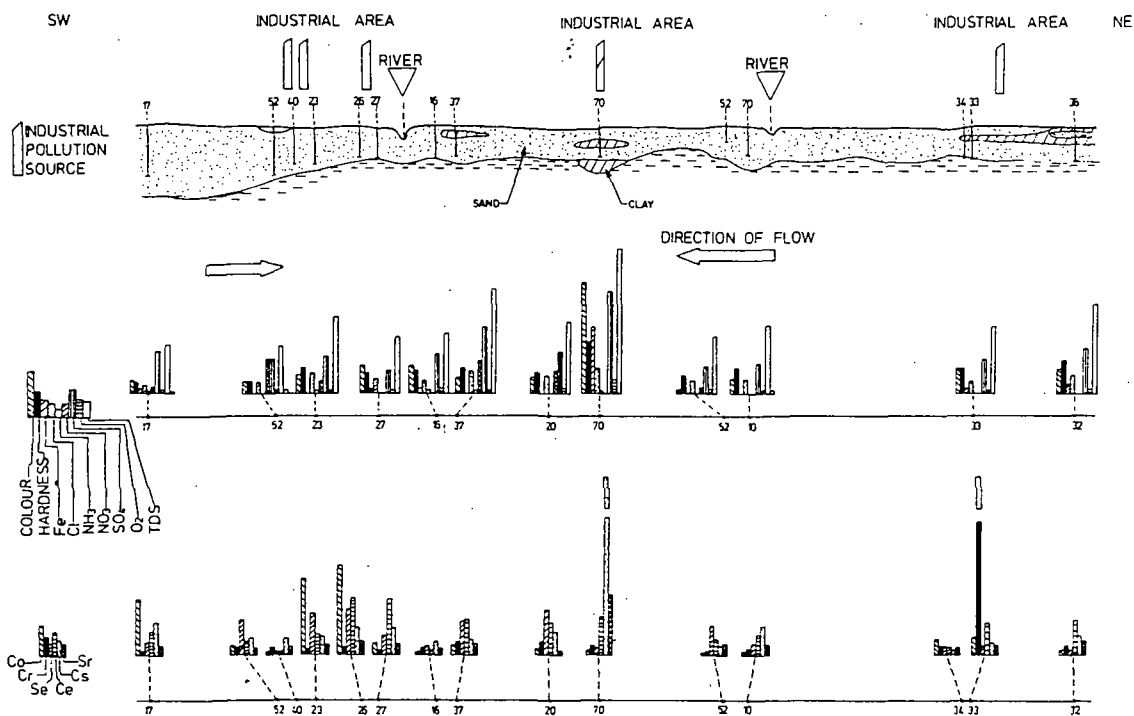


Figure II - 6.3 Cross-section through an industrial-urban area, giving a direct visual imprint of the physical and chemical properties and trace element compositions of sampled wells. Fairly good correlation is evident. The location of pollution sources is reflected selectively in high trace element concentrations in wells.

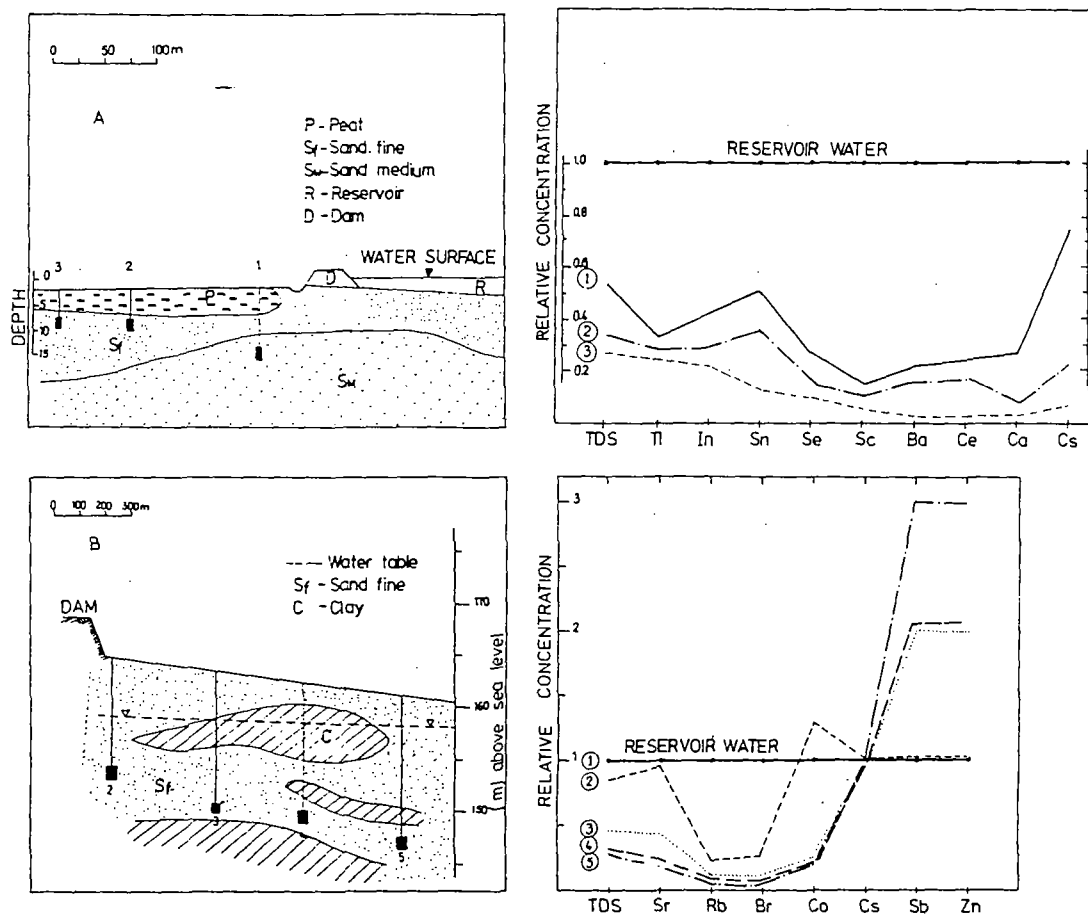


Figure II - 6.4 Direct input of polluted waters to aquifer
 a - seepage from waste-storage reservoir. Diagram shows ground water composition with respect to reservoir water.
 b - leakage from flotation reservoir. Diagram shows the trace element composition related to reservoir water. Sr, Rb, Br, Co are in excess in reservoir water. Zn, Sb dominate in ground water. Sampling points are shown in cross-section.

antimony are in excess in the ground water. The crossing point shows the same concentration of cesium.

II-6.4.2 Contamination from areal sources

Selective movement of trace elements in ground waters can be seen on the concentration diagram Figure II-6.5A obtained for a sand aquifer in Kaszubska Valley, North Poland. The aquifer is about 50 metres in depth, and recharged from nearby highlands. Point 7 represents several wells simultaneously pumped for water supply. The water was of good quality and no sign of pollution has been found. However, in the vicinity several pollution sources have been observed. In the area of wells No. 1, 2, 3, 4 an agricultural enterprise was located. The western part of the valley was cut by a municipal sewage channel. An observation of the diagram makes it evident that the concentration lines have different plots, as on the previously presented diagrams. The lines diverge showing selective movement of trace elements in ground waters. Concentrations, observed in wells No. 1, 2, 3, 4 are higher compared to concentrations in well No. 7 and thus reflecting pollution movement from the agricultural enterprise. Also well No. 6 shows high concentration of chromium, due to local contamination source. On contrary, no pollution was observed from the sewage channel.

Selective movement of trace elements in urban and agricultural areas can be well observed on concentration diagrams presented in Figure II-6.5B. As a baseline the natural concentration level in unpolluted waters has been chosen. The points laying about this line indicate the movement of pollutants into ground water. It can be noted that in the industrial area cobalt moves very selectively in ground water, and also selenium in the agricultural region.

II-6.5 CONCLUSIONS

The data collected on trace-element occurrence in ground waters have given a picture of the present state of water pollution in urban-industrial areas. The trace-level analysis enables the identification of pollutant sources and facilitates the observation of pollutant movement in ground waters. The investigations carried out in urban and industrial regions have proved the practical usefulness of trace-elemental analysis in water-pollution studies.

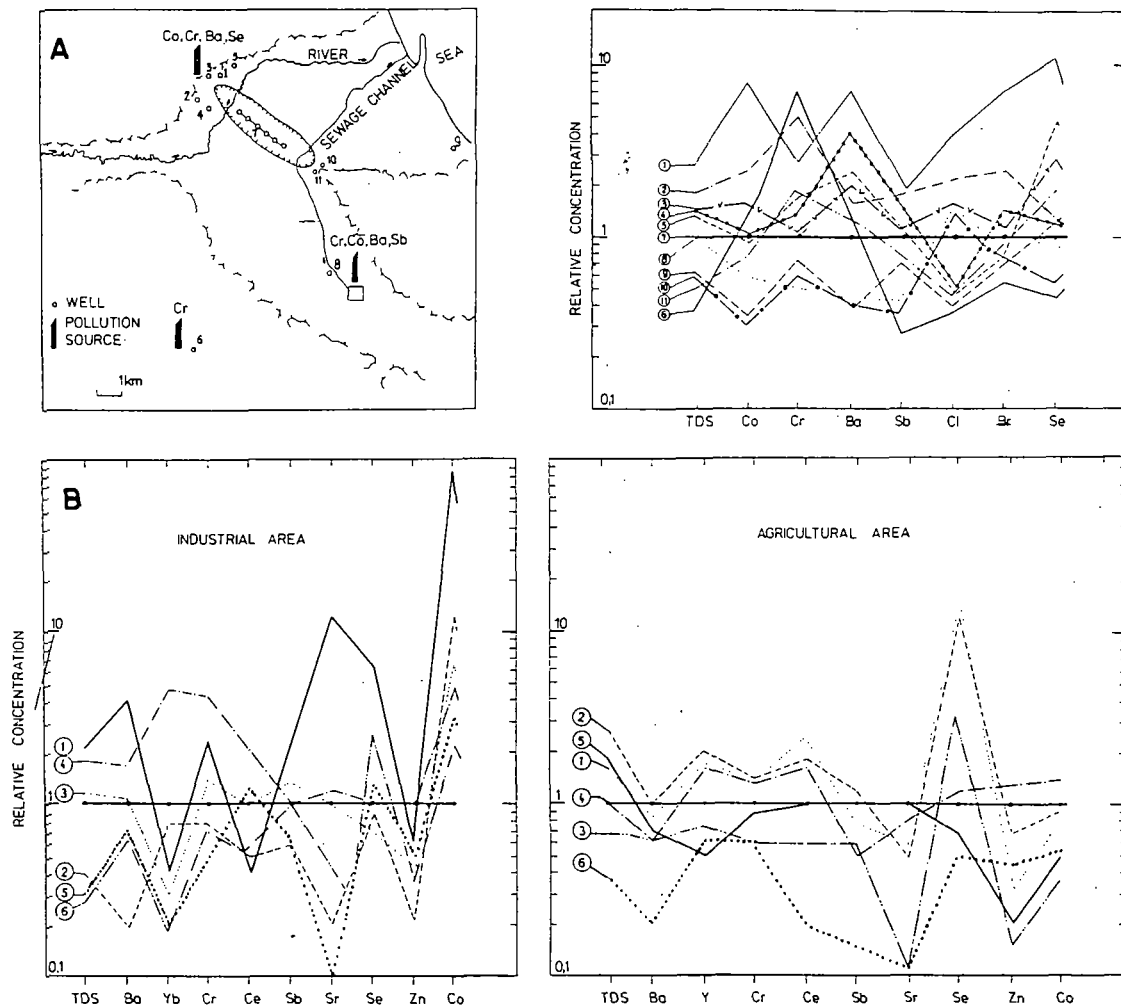


Figure II - 6.5 Infiltration input of polluted waters to aquifer. Trace element composition diagrams showing movement of pollutants in a sand aquifer.

A - Kaszubska Valley. The lines diverge indicating the selective movement of pollutants. The wells No. 1, 2, 3, 4 are polluted. The map shows schematically the location of sampled wells.

B - Vistula Valley. Concentrations are related to maximum occurring levels in unpolluted waters. Selective movement of cobalt in industrial and selenium in agricultural area can be observed.

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Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site

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Abstract—Large-volume groundwater samples were collected at the Nevada Test Site from within a nuclear detonation cavity and from approximately 300 m outside the cavity. The samples were filtered and ultrafiltered, and the filtrates and various particle size fractions were analyzed for chemical composition and radionuclide activity. In samples from both locations, approximately 100% of the transition element (Mn, Co) and lanthanide (Ce, Eu) radionuclides were associated with colloids. Their presence outside the cavity indicates transport in the colloidal form. Distribution coefficients calculated for Ru, Sb, and Cs nuclides from both field sample locations indicate equilibrium partitioning on the 0.05–0.003 μm colloids. Calculation of transport efficiencies relative to colloid mass concentrations and dissolved neutral or anionic nuclides indicates that both the cations and the radiolabelled colloids appear to experience capture by or exchange with immobile aquifer surfaces.

INTRODUCTION

RADIONUCLIDES produced during weapons testing and from military and commercial activities are among a number of human wastes requiring isolation from the biosphere. Because many radionuclides strongly adsorb to mineral surfaces, one of the key assumptions adopted in transport models is that the radionuclides, once adsorbed, are immobile. However, considerable laboratory and field evidence indicates that colloidal material is mobile in groundwater (McDOWELL-BOYER *et al.*, 1986), and it is possible that adsorbed radionuclides could be transported by these mobile colloids (CHAMPLIN and EICHHOLZ, 1968). Following a review of the literature available on colloidal transport of radionuclides in the subsurface, field data will be presented that conclusively demonstrate radionuclide transport by colloids in groundwater flowing through fractured media at the Nevada Test Site (NTS).

The potential for colloid transport is suggested because the submicrometer particles are far smaller than the pores in permeable and fractured media, and their high surface area per unit mass means that they will be effective sorption substrates. Colloid removal from solution by capture onto fixed media surfaces is controlled by the Brownian motion of the colloids and the attachment efficiency following collision. In general, for natural waters with low ionic strengths, colloid attachment to surfaces is hindered by electrostatic repulsion, but predictions based on double-layer theory underpredict observed attach-

ment by orders of magnitude (McDOWELL-BOYER *et al.*, 1986).

Some radionuclides, such as Pu and Am, are known to form aqueous colloids with dimensions of a few nanometers (DAVYDOV, 1967; BENEŠ *et al.*, 1979; CLEVELAND, 1979). These colloids have been called "true colloids", while radionuclides adsorbed onto natural colloidal matter such as clay minerals and hydrated oxides were referred to as "pseudo-colloids" (DAVYDOV, 1967; BENEŠ *et al.*, 1979). According to these definitions, a natural colloid becomes a pseudo-colloid when a radionuclide adsorbs to it. Although the chemical and physical form of radionuclides associated with colloidal material is important, the distinction between true and pseudo-colloids is inappropriate for particle-oriented rather than nuclide-oriented studies and is awkward for application to a broad range of problems. We adopt and recommend a definition of colloids based on their physical properties (i.e. subject to Brownian motion, with a size between 0.001 and 1 μm) and not on their chemical history or the scientific discipline of their observer.

The sources and properties of colloids that could transport radionuclides in natural and engineered systems are important. APPS *et al.* (1982) distinguish two processes for forming suspended colloids: (1) condensation or homogeneous nucleation of particles from dissolved species when a mineral phase is supersaturated, and (2) release of particles from bulk material into a suspension of particulate solids. Release of particles from a bulk material can include

a number of separate processes: (a) disruption of fragile aggregates by changes in ionic strength or hydrodynamic force, (b) mechanical grinding of mineral surfaces, (c) mechanical disruption of secondary minerals present at mineral surfaces, and (d) release of less soluble colloids by dissolution of a more soluble matrix surrounding these colloids. Disaggregation resulting from recharge with low ionic strength water has been held responsible for the release of clay minerals into groundwater (NIGHTINGALE and BIANCHI, 1977) and for increases in virus concentrations in well waters following rainfall events (LANCE and GERBA, 1982). SIMMONS and CARUSO (1983) discuss mineral deposition and fracturing, and VELBEL (1986) presents a review of feldspar-weathering mechanisms that can include the formation of secondary minerals such as clays. Considerable research is also being conducted on the release of colloids when glasses dissolve (SALTELLI *et al.*, 1984; SHADE *et al.*, 1984; and LUTZE *et al.*, 1983). These results indicate that submicrometer colloids can easily be released from mineral and glass surfaces that are chemically, hydrodynamically, or mechanically stressed. A related subject is the possible involvement of colloidal transport in the formation of ore bodies (HORZEMPA and HELZ, 1979; GIBLIN *et al.*, 1981).

In spite of the existence of submicrometer colloids in natural systems, there have been few studies of contaminant adsorption to colloids of this size, primarily because it is experimentally far easier to use large particles that can be efficiently separated from the solution. The presence of submicrometer colloids is known to interfere with radionuclide and organic contaminant adsorption onto micrometer and larger particles. Following conventional filtration or centrifugation of large particles, the amount of contaminant apparently remaining in solution is observed to correlate with "nonsettleable particles" or "colloidal organic carbon" concentrations (SHEPPARD *et al.*, 1980; GSCHWEND and WU, 1985; BAKER *et al.*, 1986; HIGGO and REES, 1986).

One problem associated with the application of data and methodology developed from adsorption measurements on micrometer and larger particles to colloidal adsorption is that the linear isotherm expressed as

$$q = K_d C \quad (1)$$

requires reevaluation. In Eqn (1), q is the activity of the radionuclide adsorbed per mass of solid matter, K_d is the mass distribution coefficient, and C is the equilibrium concentration of the dissolved nuclide. The isotherm relates solution activity to adsorbed activity per unit mass, so that if only the external surface area is accessible for adsorption, smaller particles would be expected to show a higher apparent K_d than larger particles because of their greater specific surface (area per unit mass). JAMES and PARKS (1982) have summarized measurements of ionizable site densities for oxide minerals that show a relatively

narrow range of 2–20 sites per square nanometer. Adsorption onto minerals expressed as adsorbed activity per unit surface area should exhibit relatively little variation other than dependence on surface group acidity because it is the ionizable sites that participate in adsorption reactions. Because of variations in specific surface area, adsorption isotherms that are measured on micrometer and larger particles and represented according to Eqn (1) are suspect in any case and in particular may not be applicable to adsorption onto colloids.

Quite frequently in the literature there is reference to adsorption onto micrometer and large particles of species that exist as colloids. CLEVELAND (1979) has soundly denounced such an interpretation for the interaction of plutonium oxide colloids with glass surfaces. Colloid attachment is irreversible except under aqueous solution conditions that favor dissolution of the colloid, and the maximum Pu loading is controlled by the physical limit of colloid packing on a surface. Because such colloid-media associations cannot be described as ion-exchange phenomena, adsorption isotherms are completely inadequate mechanistic models. Studies of radionuclide cycling in lakes and oceans have recently acknowledged the importance of radionuclide association with colloids, and models for radionuclide attachment to settling particles are being developed based on coagulation kinetics (SANTSCHI *et al.*, 1986).

No earlier reports of field investigations directly demonstrate radionuclide migration by colloid transport. A number of field studies have observed anomalous, rapid transport of radionuclides that suggests mobile colloids are acting as carriers. TRAVIS and NUTTAL (1985) have summarized the available data and cited the reports on radionuclide transport from a low-level waste site at Los Alamos National Laboratory (LANL) where both Pu and Am migrated more than 30 m downward through unsaturated tuff over the course of approximately 30 a. Laboratory experiments on the tuff suggested that colloidal Pu and Am were responsible for the rapid migration.

Investigations of four waste plumes in groundwater at the Chalk River Nuclear Laboratories in Canada were described by CHAMP *et al.* (1984). The analytical procedures for separating γ -emitting radionuclides distinguished only four forms: "particulate" species captured on 0.4- μ m filters, and nuclides $<0.4 \mu$ m that were retained on either cation or anion exchange resins or on an activated aluminum oxide bed. For ^{60}Co , ^{95}Zr , ^{106}Ru , and ^{125}Sb , the anionic resin dominated the collection. The authors suggested that organic ligands enhanced the mobility of Co, Ce, Cs, Eu, Sb, and Zr. The detection of significant particulate nuclides on the 0.4- μ m filter was reported for ^{60}Co , ^{95}Zr , ^{106}Ru , ^{137}Cs , and ^{14}Ce . The mass of particulate matter in suspension was not reported, but because reported sampling flow rates were about 100 ml/min with 30 min of purging, the particle concentra-

tions were probably representative of groundwater conditions and not affected by near-well erosion.

An *in situ* glass-block-leaching experiment is one of the four study sites at Chalk River. Field measurements of ^{137}Cs migration indicated transport four times farther than predicted from K_d values (CHAMP and MERRITT, 1981). Soil columns prepared from undisturbed, uncontaminated cores showed Cs transport by 0.2–1.0 μm particles. There was also an indication that microorganisms were involved in particulate Cs release and transport.

There are few published data on colloid concentrations in groundwater. BARNES (1975) analyzed 0.1 μm -filtered samples from springs and oil wells for monomeric Al and Al species that would dissolve during storage for two weeks at pH 2. The acidified samples averaged 7 $\mu\text{g/l}$ greater Al concentration and indicated the presence of colloidal, microcrystalline, or polymerized forms of Al. Given Al is but one component of an Al-containing mineral phase, approximately 50 $\mu\text{g/l}$ of the $<0.1 \mu\text{m}$ Al colloids are indicated. Near a secondary sewage infiltration site GSCHWEND and REYNOLDS (1987) estimated colloid concentrations ranging from $<1 \text{ mg/l}$ to 6.5 mg/l using light scattering measurements. Preliminary results of a survey of Nevada Test Site (NTS) groundwater by the Desert Research Institute have shown that groundwaters in the Pahute Mesa drainage (both on and off NTS) have particle loadings $>0.03 \mu\text{m}$ of 0.8–6.9 mg/l , and one NTS spring was found to have about 16.4 mg/l in the 0.4–0.03 μm size range (R. JACOBSON, pers. commun.). Such results suggest that

weapons-generated radionuclides adsorbed onto colloids could be transported by groundwater flow at the NTS, particularly because the ionic composition of NTS groundwater is not expected to coagulate clay colloids (APPS *et al.*, 1982).

FIELD SITE

Field studies of radionuclide migration from underground nuclear tests at the NTS have been ongoing since 1974. The research is carried out through the Radionuclide Migration Program, funded and managed by the U.S. Department of Energy, with scientific participation by Lawrence Livermore National Laboratory (LLNL), LANL, the Desert Research Institute (DRI) of the University of Nevada, and the U.S. Geological Survey (USGS). A number of detonation sites are being monitored by this program (BUDDEMEIER and ISHERWOOD, 1985), but our focus is on the Cheshire event (U20n) fired on 14 February, 1976, with an announced yield in the 200–500 kiloton range. The site is on the Pahute Mesa within the Silent Canyon Caldera. The device was detonated at a depth of 1167 m in a formation consisting primarily of fractured rhyolitic lavas; the pre-shot water level was at a depth of 630 m. Figure 1 shows a vertical section of the installation and stratigraphy and the hydraulic head as a function of depth in a nearby well (U20-a No. 2 water well) prior to detonation.

The Cheshire site is of interest to the Radionuclide Migration Program for three reasons. First, it is the

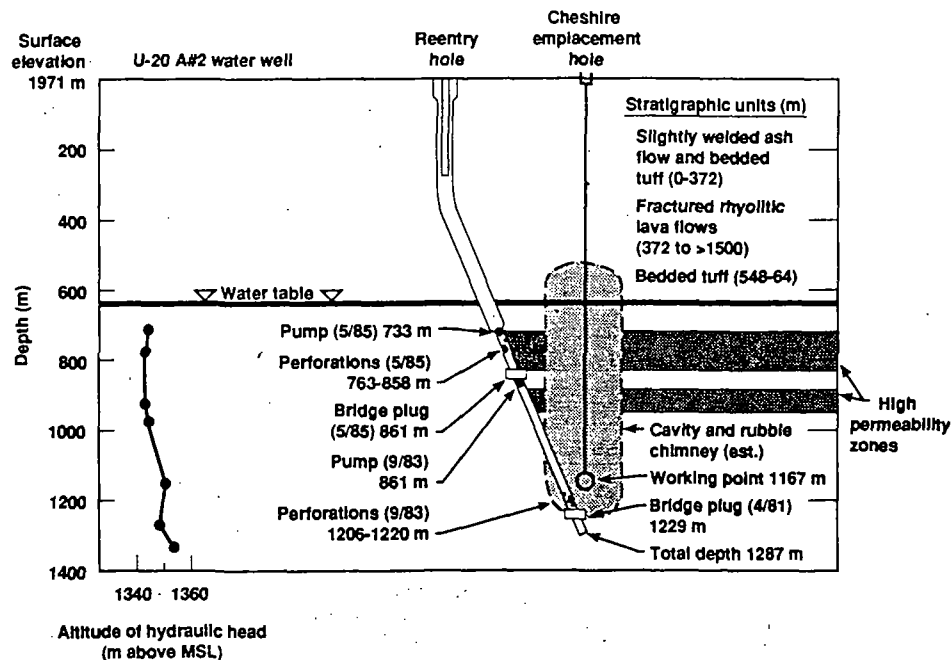


FIG. 1. Vertical section of Cheshire experimental site showing sampling locations, hydrogeological stratigraphy, and hydraulic head with depth (BLANKENAGEL and WEIR, 1973). Horizontal dimensions are not to scale.

only study site in fractured lava and tuff as opposed to alluvial or carbonate aquifers. Second, the detonation was more recent and larger than most of the other shots under investigation, thus providing a larger source term and a better opportunity to study the behavior of the short-lived radionuclides. Finally, the site is only 8 km from the western boundary of the NTS in a permeable formation with a water table trending southwest; this site is therefore a potential candidate for off-site transport of radionuclides.

Subsurface access to the detonation cavity was by means of a slant-drilled re-entry hole that was eventually cased and perforated within the cavity. Cavity water was intermittently pumped and sampled. In May 1985, the well was plugged and re-perforated as indicated in Fig. 1, and pumping was resumed. The new perforations were in zones with higher permeability, approximately 250 m above the estimated upper boundary of the original detonation cavity and about 100 m laterally downgradient. Local groundwater is expected to flow upward through the cavity and chimney, driven by the vertical hydraulic gradient, and then horizontally through the permeable zones toward the second set of perforations. For the mesa as a whole, WADDELL (1982) estimated transmissibility to be 9.4×10^{-4} m²/s, and a pump test near the Cheshire site indicated a transmissibility of 2×10^{-2} m²/s (BLANKENNAGEL and WEIR, 1973). The uncertainties in these values, especially as applied to specific strata in a heterogeneous formation, hinder precise estimation of groundwater transit times from the cavity to the external sampling location.

SAMPLING AND ANALYSIS

Samples were collected from a pressurized manifold connected to the pump outlet at the well head. To minimize near-well and casing effects on the samples and hydraulic disequilibrium effects, samples were not collected until a minimum of several well volumes had been pumped; the casing volume below water table is 3.5×10^{-4} l or $\sim 10^4$ gal. Pumping rates were generally around 120 l/min (30 gal/min). During the course of pumping from both the cavity and the

formation locations, water was sampled and measured in the field for pH, temperature, dissolved oxygen, conductivity, and alkalinity. Small (1–5 l) samples were collected at intervals and returned to the laboratory for chemical or radionuclide analyses. The large-volume water samples that are the focus of this report were collected in new, plastic-lined ~ 200 l (55-gal) drums, sealed, and shipped at ambient temperatures to LLNL.

The samples reported on in this paper were analyzed as part of a progressively evolving investigation initiated after significant levels of insoluble, strongly sorbing radionuclides were observed in water samples processed with conventional (0.45 μ m) filtration. Because of the evolutionary nature of the study, the samples were not all treated identically; this section describes the procedure common to all of the samples; Appendix A details the specific individual procedures.

In the laboratory, the samples were well mixed with a mechanical stirrer and pumped through a sequence of conventional filters. Table 1 shows the filtration treatments of the various samples; Appendix A provides details of filter types and treatments. Filters were packed into standard containers and counted on low-background Ge(Li) detectors. After being counted separately, the filters were ashed and the ashes representing all of the filters from a given barrel were combined and recounted as a check on the total filterable activity.

Selected filtered samples were ultrafiltered through a Millipore XX42 Pellicon cassette system with either a 100,000 or a 10,000 MWU ultrafilter (nominal pore sizes 0.006 and 0.003 μ m, respectively). The ultrafiltration typically produced approximately 200 l of ultrafiltrate (that which passed the ultrafilter) and a few hundred ml of retentate containing the colloids that did not pass the ultrafilter. The filtrates and retentates were evaporated to dryness, weighed, packed in standard-volume counting containers, and gamma-counted. All gamma spectral data were processed using the GAMANAL computer code (GUNNINK and NIDAY, 1974). Laboratory tests showed that there was no significant loss of sample activity to either container walls or to the ultrafilter (BUDDEMEIER and ISHERWOOD, 1985). Because of the large surface areas involved in these tests, we believe that the results indicate that sorption onto the conventional filters was also negligible.

All samples were analyzed for ³H by liquid scintillation counting techniques. Selected samples collected at the same time as samples B-4 and B-5 were also analyzed for ⁹⁹Tc (SILVA *et al.*, 1986, 1987). Aliquots of various samples and stages of filtration were analyzed for cation content by inductively coupled plasma optical emission spectroscopy (ICP-OES) and for anions by ion chromatography. Selected samples of dried ultrafiltrates and retentates were also

Table 1. Sample descriptions

Sample	Location	Date collected	Cumulative water pumped (l)*	Filters (retention size μ m)†
B-1	Cavity	9/8/83	2.1×10^5	1.0–0.45–0.20–0.006
B-2	Cavity	9/9/83	5×10^5	0.45
B-3	Cavity	10/23/84	1.1×10^7	1.0–0.45–0.20
B-4	Cavity	10/23/84	1.1×10^7	1.0–0.45–0.45–0.20–0.05–0.003
B-5	Formation	5/28/85	1.4×10^7	1.0–0.45–0.20–0.05–0.003
			$(1.04 \times 10^6)^\ddagger$	
B-6	Formation	5/28/85	1.4×10^7	1.0–0.45–0.20–0.05–0.003
			$(1.05 \times 10^6)^\ddagger$	

* Total volume pumped subsequent to installation of cavity sampling location.

† 0.006 and 0.003 μ m filters are 100,000 and 10,000 MWU ultrafilters, respectively.

‡ Cumulative volume pumped at formation location after relocation of perforated interval and pump.

analyzed by X-ray diffraction (XRD) to determine the dominant mineral phases present and by X-ray fluorescence (XRF) for elemental composition.

All reported concentrations (mg/l) and specific activities ($\mu\text{Ci}/\text{ml}$) were based on the original sample volume before processing, and all activities were decay corrected to the time of detonation ($T_0 = 14$ February 1976). This normalization was necessary in order to compare activities measured at different times, but it means that the zero-time activities reported for the short-lived nuclides may be orders of magnitude greater than the actual measured values. For ease of comparison, nuclide half-lives are tabulated with the activity data.

The GAMANAL code provides calculated standard deviations based on counting statistics, and provides an upper limit value if gamma-ray peaks of the requisite energies are not resolvable from background. These calculated uncertainties are appropriate for samples which approximate a massless point source, but are inadequate for assessing the experimental uncertainties associated with larger samples (e.g. filters and salt samples). These calculations require the use of assumptions about sample homogeneity and self-absorption that may introduce additional uncertainties. Experimental tests have shown that $\pm 25\%$ is a satisfactorily conservative estimate of the total uncertainty (one standard deviation) in the measured activity of such samples. In propagating the uncertainties reported in this paper, we used the larger of the GAMANAL-calculated uncertainty or 25% of the measured activity.

RESULTS

Figure 2 shows the history of ^3H activities as a function of volume pumped and pumping times. Activity values indicate trend lines for both the cavity and formation samples that are similar and only

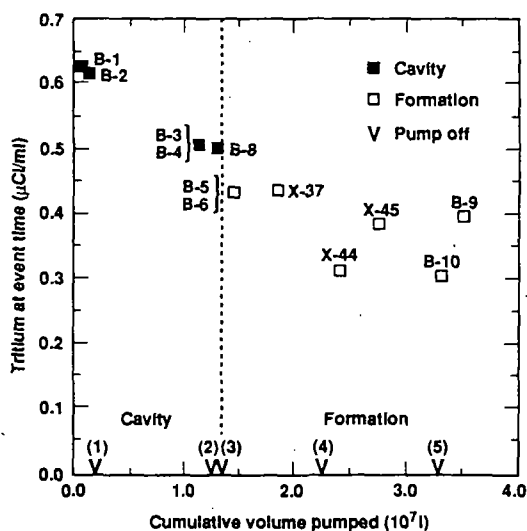


FIG. 2. Pumping history and ^3H activity at the Cheshire site. Tritium counting uncertainties are typically $< 1\%$. Samples coded X are small-volume samples analyzed for ^3H only. Samples B-7 through B-10 are large-volume samples not fully processed at the time of publication. Coded symbols represent intervals when pump was off: (1) 9/9/83 to 8/1/84; (2) 10/25/84 to 4/25/85; (3) 5/14/85 to 5/23/85; (4) 7/20/85 to 9/11/85; (5) 10/1/85 to 10/8/85. (No water has been pumped since 11/7/85.)

slightly offset (see THOMPSON, 1987, for a similar presentation of LANL data). The total volume pumped probably did not exceed 10% of the cavity water contents, and cannot account for the observed decrease in activity (THOMPSON, 1986). Natural flushing of the cavity by the groundwater flow system is indicated by the secular trends in the data, the similarity between cavity and formation activities of dissolved nuclides, and the observation that the measured activities are far less than the predicted source term (THOMPSON, 1986, 1987). Preliminary data from a new test well several hundred meters downgradient show ^{125}Sb and ^3H activities in the uppermost water-bearing zone that are similar to the activities reported here (LLNL unpublished data). This confirms the interpretation that hydrological transport is occurring in this vicinity. The ^3H activity values deviate from a smooth curve by considerably more than detection uncertainties ($\leq 1\%$) can explain. Because ^3H is a generally conservative tracer and is present at levels too high to be affected by sample contamination, we believe the scatter reflects spatial and/or temporal variability in the formation water. The scatter may also be amplified by the effects of intermittent pumping or of integrated sampling over a substantial vertical interval of a fractured aquifer.

Results from the six large-volume samples designated B-1 through B-6 (see Table 1 and Appendix A) are emphasized here, supported as appropriate by data from other samples and reports. BUDDEMEIER and ISHERWOOD (1985) and MARSH *et al.* (1988) provide additional data and experimental information. For convenience and consistency of notation, ultrafilters are identified by their nominal equivalent pore size. Wellhead measurements indicated that cavity water had a pH of 8.6, a dissolved oxygen concentration of approximately 3 mg/l, and a temperature of 40–42°C when stabilized by protracted pumping. For the formation samples, the field pH was 8.4 with 5 to 6 mg/l dissolved oxygen and a temperature similar to the cavity. The elevated groundwater temperatures are consistent with other observations on Pahute Mesa (CLAASSEN, 1976), and are believed to be due to natural geothermal sources rather than to nuclear detonation effects.

Laboratory analyses showed that the groundwater is a sodium bicarbonate type with a substantial concentration of silica (BUDDEMEIER and ISHERWOOD, 1985; MARSH *et al.*, 1988). Chemical and radiochemical differences between samples were frequently at or beyond the limits expected from analytical uncertainties and smoothed trends in the data. As with the ^3H variations, this probably reflects spatial or temporal variability in the formation water, but may also be due in part to the influences of the rate and duration of pumping in particle recovery.

Total dissolved solids (TDS) and colloid concentrations were estimated from dried ultrafiltrate and retentate samples. Table 2 summarizes these results and indicates the considerable mass of submicrom-

Table 2. Dissolved and colloidal material in Cheshire samples

Sample	Location	TDS (mg/l)	Colloid size range (μm)	Colloid mass concentration (mg/l)
B-1	Cavity	260	0.20–0.006	55
B-2	Cavity	(260)*	0.45–0.006	(63)*
B-3	Cavity	(265)*	0.20–0.003	(35)*
B-3	Cavity	(265)*	0.20–0.05	(25)*
B-4	Cavity	265	0.05–0.003	10.1
B-5	Formation	217	0.05–0.003	4.6
B-6	Formation	219	0.05–0.003	4.3

* Indicates an assumed value based on samples collected close in time to the indicated sample.

eter colloids present in these pumped groundwaters. Because ultrafiltration was assumed to exclude all colloids, the derived ultrafiltrate is a measure of the TDS. Some extrapolation was necessary; this is indicated by the numbers in parentheses in Table 2. For example, because the ultrafiltration TDS was not available for sample B-2, the value from B-1 was assumed. Similarly, sample B-3 was collected on the same date as B-4, so the TDS of 265 mg/l from sample B-4 was assumed for sample B-3. Dried retentate samples provided estimates of colloid mass concentration. The 194.5 l of 0.05 μm -filtered sample B-4 was ultrafiltered, producing a retentate volume of 0.245 l with a dried mass of 2.04 g. Assuming the retentate has the same TDS value as the ultrafiltrate provides the estimate that 10.1 mg of 0.05–0.003 μm colloids are present per liter of the original sample. Samples with different filtrations prior to ultrafiltration provide colloid masses in the various size ranges given in Table 2. It is of interest to note that these original samples were not cloudy in appearance despite the high colloid concentrations.

Data on radionuclide activities separated by various stages of filtration and ultrafiltration and remaining in the filtrates are compiled in Appendix B (Tables B-1 through B-6 for samples B-1 through B-6, respectively). The ^{40}K is a naturally occurring isotope with virtually no production by the detonation; all other radionuclides are detonation products. Total activities and the fraction dissolved are based on summations of the individual fractions, with limit values treated as zeros. Where filters were all below detection limits but the ashed composite yielded a positive value, the ash value was used. Sample weights, volumes, and the details of processing are given in Appendix A. Sample B-2 was the first sample processed, and significant activities of the low-solubility, adsorbing nuclides Mn, Co, Ce, and Eu passed through the 0.45- μm filters. This unexpected result provided the impetus for studies of filtration methods to separate dissolved from particle-associated nuclides, and of particle-associated transport in general.

Sample B-1 included the ultrafiltration step for the first time, and the analysis indicated that colloidal

material in the size range of 0.20–0.006 μm contained a significant fraction of the total activity of the radionuclides Mn, Co, Cs, Ce, and Eu. The final configuration for analysis of samples B-4 through B-6 included the 0.05- μm step to provide further information on radionuclide partitioning on the smaller colloids and single-pass filtration through the string of conventional filters.

Different radioisotopes of the same element typically have different precursors and, in some cases, different production mechanisms (e.g. activation *versus* fission). Comparison of isotopic behaviors can therefore serve not only as a check on the collection and analytical procedures, but also as an indicator of the degree of geochemical equilibrium within the system. In general, radioisotopes of the same element are very similar in their distribution of activities among filter sizes. For example, in sample B-4 the fractions of total activity collected on the 1.0- μm filter were 0.111 and 0.116 for ^{134}Cs and ^{137}Cs , respectively, and a similarly small variation was observed for the three Eu isotopes: 0.359, 0.364, and 0.345. Because ^{134}Cs , ^{152}Eu and ^{154}Eu are (n, γ) neutron activation products, ^{137}Cs is a fission product with volatile precursors, and ^{155}Eu is a fission product derived from refractory precursors, these results indicate that chemical and physical (sorption) equilibration occurs on a time scale short compared to the time elapsed since detonation. The results further suggest that potentially fractionating transport mechanisms (e.g. vapor phase injection) associated with the detonation or immediate post-detonation environment must be of minor importance compared to long term hydrological transport. These results also indicate the absence of any real or apparent fractionation effects in the sample processing and counting procedures.

Both the total activities and the particulate activity distributions, like the chemical analyses, suggest the existence of sample-to-sample variations that are greater than can be attributed to analytical uncertainty or the long-term trends in the data. The discussion that follows concentrates on ratios and large-scale systematic differences that are insensitive to the level of noise in the experimental results.

X-ray diffraction studies were undertaken for

Table 3. The results of X-ray fluorescence analysis of sample B-4

Element	Concentration passing 0.05 μm filter ($\mu\text{mg/l}$)	Fraction colloidal 0.05–0.003 μm size range
K	735	0.36
Ca	784	0.028
Mn	31	0.18
Fe	140	0.40
Ni	8.6	0.023
Cu	2.9	0.064
Zn	530	0.011
As	13.1	0.016
Br	37	0.004
Rb	7.0	0.28
Mo	10.8	0.004
Cs	<1.5	>0.11
Ba	8.7	0.24
La	<1.5	>0.13
Ce	<2.2	>0.40
Pb	12.5	0.26

sample B-4 to gain some insight into the mineral composition of the colloids. The dried ultrafiltrate was composed of evaporite salts (halite, trona, aragonite) consistent with the dissolved species present, while the ultrafilter retentate solids in the 0.05–0.003 μm range were dominated by quartz and (Ca, K) feldspars. Approximately 10% of the dried ultrafilter retentate solids could not be identified by X-ray diffraction, but could be clay minerals formed as secondary minerals during feldspar weathering (VELBEL, 1986). Fourier-transform infrared spectroscopic characterizations being carried out at the Desert Research Institute tend to support the hypothesis that clays are present in the colloid fractions (R. JACOBSON, personal communication).

The distribution of trace elements between the ultrafilter retentate and the filtrate was measured for sample B-4 by X-ray fluorescence. Table 3 lists the elements detected, the total concentration per liter of groundwater passing the 0.05 μm filters, and the fraction of that element that is present on 0.05–0.003 μm colloids. For K, Mn, Fe, Rb, Cs, Ba, La, Ce, and Pb, between 10 and 40% of the amount of each element passing the 0.05 μm filter is present on the small colloids. Detectability problems hinder a comparison of radionuclide association on colloids with elemental association, but X-ray fluorescence indicates that 36% of the K passing through the 0.05- μm filter was colloidal compared to 32% of ^{40}K . For ^{134}Cs and ^{137}Cs , 18% and 12%, respectively, of the activity passing the 0.05- μm filters was colloidal, while X-ray fluorescence indicates >11% colloidal. The results are consistent with each other and with chemical expectations within the uncertainties of these methods, and indicate that the observed colloidal associations of radionuclides are representative of a larger phenomenon of trace element partitioning.

DISCUSSION

Radionuclide transport from the cavity to the formation is dependent on both physical and chemical factors. Figure 3 compares the ratio of formation (sample B5) to cavity (sample B4) total activity with the dissolved fraction for each nuclide in the cavity sample. Also included are ranges of ratio estimates for two nuclides conventionally treated as conservative (dissolved) tracers: ^3H and ^{99}Tc . The ^{99}Tc point is based on the data presented by SILVA *et al.* (1987) for samples corresponding to B-4 and B-5; the ^3H ratio and range was estimated by averaging the LLNL and LANL (THOMPSON, 1986) analyses of samples collected within a week of each of the two large-volume samples. Although there is a slight overlap in the ranges, the ^3H appears to be less diluted ($86 \pm 7\%$ of the cavity value) at the formation sampling point than does the Tc ($64 \pm 21\%$). This may reflect different transport characteristics in the immediate post-detonation environment (e.g. vapor-phase transport) or it may be an artifact of the untested assumption that the two nuclides are in fact completely dissolved, conservative tracers.

For the Co, Ce, and Eu nuclides that are >98% associated with colloids, the activity at the formation location is <4% of the cavity level, indicating significant colloid removal during solution transport. ^{54}Mn has a formation/cavity ratio of 0.20 ± 0.21 ; because of the large uncertainty, the value was not plotted in Fig. 3. Because the formation colloid concentrations (Table 2) are approximately 50% of the cavity value and the particulate activities are approximately 2.5% of cavity activities, it is evident that the loss and

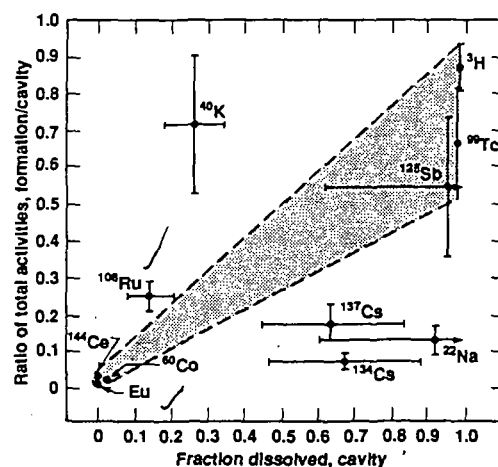


FIG. 3. Ratio of formation (B-5) to cavity (B-4) total radionuclide activities as a function of dissolved fraction of total activity at the cavity location. Error bars represent cumulative counting uncertainties; data from Tables B-4–B-6. Europium values are an average of the three Eu isotopes measured. The shaded area represents the region in which data should fall if the nuclide transport represents a simple combination of the pure particulate (^{60}Co , ^{144}Ce , Eu) and conservative (^3H , ^{99}Tc) dissolved cases.

acquisition of colloidal particles by the moving groundwater must be a dynamic process. If there were no chemical exchange between dissolved nuclides and suspended colloids or between dissolved nuclides and fracture surfaces, then the other nuclides ought to fall in the shaded range in Fig. 3 that connects the "completely particulate" with the "completely dissolved" nuclides. The ^{106}Ru and ^{125}Sb values fall reasonably close to the range of values specified by the mixing curve of Fig. 3. Although a large fraction of the total ^{106}Ru is in the particulate form, both Sb and Ru in the dissolved form are expected to exist as anionic species under the chemical conditions of NTS groundwater, and should behave in solution much as does ^{99}Tc (BUDDEMEIER and ISHERWOOD, 1985).

The other nuclides that exist at least partly in dissolved form do not fall in the shaded range of Fig. 3. For ^{22}Na , ^{134}Cs and ^{137}Cs , there is lower activity in the formation compared to that expected if only physical dilution and colloid removal were operating. This suggests either adsorption of dissolved contaminants to fracture surfaces or exchange of a radionuclide with a naturally occurring stable ion. The ^{40}K values represent naturally occurring levels, and provide an indication of the chemical variability of natural constituents in both the particulate and dissolved forms.

Adsorption and desorption of nuclides can be quantified for nuclides with detectable activities in the dissolved fraction and the 0.05–0.003 μm particle size range for which we have measured colloid mass concentrations (Table 2). The K_d values for ^{106}Ru , ^{125}Sb , ^{134}Cs and ^{137}Cs are calculated from Eqn (1) and listed in Table 4 for the last cavity sample and the two formation samples. Uncertainties are one standard deviation, calculated from counting uncertainties only. The calculated distribution coefficients for all nuclides are identical within the calculated uncertainties for the cavity sample and the first formation sample. Cesium adsorption onto montmorillonite has a measured K_d of $4.5 \times 10^3 \text{ ml/g}$ at 26°C in 2 mM NaCl (SILVA *et al.*, 1979), a Na concentration similar to that measured in groundwater at this site (3 mM). This is in satisfactory agreement with the field values, and is consistent with the hypothesis that aluminosilicate clays are a significant component of the 0.003–0.05 μm colloid fraction. Formation sample B-6 was consistently somewhat lower in K_d values for all the nuclides; the sample had solution activities and

particle loading similar to B-5, but lower particulate activities. As discussed above, we cannot at present identify a reason for these between-sample variations.

The results obtained in this study are critically dependent on filtration for size separation of colloids from solution. For groundwater samples containing colloids in dilute concentrations of the order of milligrams per liter, there are no alternative procedures for concentrating the colloids to the extent needed for radionuclide detection. We recognize a number of well-known problems with filtration for size characterization, but we conclude that these potential problems do not compromise the fundamental findings of this study. An overall evaluation of colloid-solution separation techniques for trace-metal speciation studies has been provided by DEMORA and HARRISON (1983). For the type of conventional (depth) filters used in this work, particle retention efficiency is only weakly dependent on particle size near the stated filter pore size. JOHNSON and WANGERSKY (1985) have shown that filter removal efficiency also depends on colloid stability; particles much smaller than the filter pore size were removed under the high ionic strength conditions of seawater, but there was no removal when the particles were suspended in distilled water. Another phenomenon hindering size separation by filtration is the partial clogging of filter pores as material is retained (DANIELSSON, 1982). Comparison of results between 0.45 μm etched Nuclepore filters (B-2, Table 4) and bag-type filters (B-3, Table 5) indicates that some clogging may have occurred in the Nuclepore-filtered sample.

The intensity of fluid mixing, which could break up fragile aggregates into smaller aggregates or primary particles and result in an apparent shift of particles into the smallest size class is also an issue with filtration and ultrafiltration. Such disaggregation is not expected to increase the specific surface area for adsorption because new surfaces are not being formed. This sort of disaggregation may have occurred in sample B-1, which was ultrafiltered by repetitively cycling the fluid through the entire filter string. The conventional filters for this sample consistently contained a smaller fraction of the total activity than was the case for the other cavity samples, which also serves to confirm that sorption of dissolved nuclides into the filters was not a major problem.

Because colloid transport processes are size depen-

Table 4. Calculated K_d values (ml/g) for 0.05–0.003 μm colloids

Nuclide	Cavity B-4	Formation	
		B-5	B-6
^{106}Ru	$1.1 \pm 0.4 \times 10^3$	$1.7 \pm 0.6 \times 10^3$	$0.39 \pm 0.14 \times 10^3$
^{125}Sb	$1.3 \pm 0.5 \times 10^3$	$1.3 \pm 0.5 \times 10^3$	$0.41 \pm 0.14 \times 10^3$
^{134}Cs	$7.6 \pm 3.0 \times 10^3$	$5.3 \pm 3.5 \times 10^3$	—
^{137}Cs	$10.1 \pm 4.1 \times 10^3$	$8.7 \pm 3.1 \times 10^3$	$2.6 \pm 0.9 \times 10^3$

dent, any procedure that alters colloid sizes would give results that could not be used for quantitative prediction of transport. We point out, however, that the effects of the filtration problems discussed above would be primarily on the size distributions of colloids, not on the partitioning of materials between the total colloid loading and the dissolved phase. NTS groundwater is oxygenated and low in organic matter, a substantial proportion of the colloidal material is apparently composed of stable, natural minerals, and both the K_d estimates and the isotopic comparisons indicate an equilibrated system. The samples are therefore expected to be reasonably stable during processing and storage. Our experience to date with Cheshire groundwater samples indicates that serial filtration and ultrafiltration provide reasonably consistent results that are suitable for the qualitative and semi-quantitative investigation of colloid characteristics and transport and for the monitoring of radionuclide concentrations.

These results raise a number of issues related to sampling, colloid characterization, colloid transport, and modeling of trace element and radionuclide migration in fractured media. Samples collected from subsurface environments are initially influenced by drilling and well development activities which are mechanically, chemically, and hydraulically disruptive. It is not clear how these factors alter colloid generation, resuspension, and transport. At the Cheshire site, the time between initial drilling and sampling was 7 a. However, casing tests, shot perforation, etc. prior to the sampling produced some demonstrable effects on the characteristics of initial samples BUDDEMEIER and ISHERWOOD, 1985). In addition to the problems of groundwater and colloid sampling, this aquifer is repeatedly subjected to blast-induced pressure pulses that could erode colloids attached to fracture-wall surfaces.

Groundwater was pumped at approximately 120 l/min (30 gal/min) from a perforated interval more than 20 m long, and at least 2×10^5 l were pumped after startup and prior to collecting large-volume samples. We believe that the aquifer was not hydraulically stressed under these conditions and that the effects of near-well environmental perturbations were minimized. For these same reasons, however, we cannot claim that the samples represent either specific naturally occurring aquifer characteristics or groundwater flow conditions. The pumping rate used necessarily induced flow velocities substantially greater than normal groundwater velocities, especially in the immediate vicinity of the casing perforations. It is possible that this may have induced artificially higher colloid loadings in the pumped samples than in the actual groundwater. We assert, however, that neither the volume extracted nor the pumping rates can account for the presence of the labelled colloids at the formation sampling location. The existence of potentially mobile radio-labelled colloids at both locations demonstrates the reality of

hydrological transport. Further, we note that artifacts should diminish with pumping time and volume as the zones subject to high pore velocities are cleaned out (analogous to well development). The ratios of the various nuclides to ^3H in different samples at the same location vary only over a factor of about two, which suggests that our determinations are probably valid at least at the order-of-magnitude level.

The colloids collected in the NTS groundwater at the Cheshire site are incompletely characterized. Obviously, better colloid characterization is necessary, as is better understanding of the relations between sample characteristics and *in situ* groundwater characteristics. However, due to dilute colloid concentration, heterogeneous distributions in size, chemistry and mineralogical composition, and inaccessibility of the groundwater environment, advances in experimental techniques are needed.

Because planning for radioactive waste disposal requires prediction of radionuclide migration for thousands of years, some predictive modeling is required. Although a number of colloid transport models for fractured media have appeared in the literature (TAVIS and NUTTAL, 1985; BONANO and BEYELER, 1985), there is as yet much uncertainty regarding water flow, conservative tracer transport, and mechanisms of colloid generation, deposition, and erosion. Extensive model development activities are premature without both a fundamental understanding of mechanism and data collection efforts in the laboratory and the field for model calibration and verification.

SUMMARY AND CONCLUSIONS

Filtration and ultrafiltration studies were carried out on groundwater samples from a seven-year-old nuclear detonation cavity at the NTS and from the fractured lava and tuff formation hydrologically down-gradient from the cavity. Substantial loadings of submicrometer colloids and significant radionuclide concentrations were found at both sampling locations, with values in the formation water somewhat lower than those in the cavity. A substantial fraction of the radioactivity at both locations was associated with colloidal particles ranging in size down to $0.003 \mu\text{m}$; lanthanide and transition metal radionuclides were essentially completely particulate (ultrafilterable). Based on the data presented, we conclude that:

- (1) There is a strong association between colloidal solids and radionuclides, particularly in the case of elements that are strongly sorbing and/or insoluble under groundwater conditions.
- (2) Both the dissolved and colloidal radionuclide species undergo hydrological transport through the fracture-flow system.
- (3) A substantial proportion of the radionuclides

associated with suspended colloids pass through the conventional (0.1–0.45 μm) filters traditionally used to distinguish between “particulate” and “dissolved” species.

In addition to these primary conclusions, supporting studies and data interpretation point toward further conclusions that are not rigorously proven, but that we consider sufficiently interesting and important to put forward as hypotheses that merit further testing. These points are:

(4) Measurements indicate that most of the colloidal material consists of natural minerals. There is some evidence that the high colloid concentrations observed are not unique to the specific study site, but there is no basis on which to decide whether these levels are natural or are elevated because of the continued underground testing of nuclear explosives at the NTS.

(5) Chemical analyses, isotopic comparisons, and K_d calculations all suggest that the radionuclides have chemically equilibrated with the groundwater system, and that their behavior is representative of their stable analogs and of trace element geochemistry in general.

(6) Colloidal nuclides and soluble cations are transported less efficiently than soluble neutral or anionic species, indicating that both colloids and cations experience some additional process of loss to or exchange with the aquifer during hydrological transport.

We feel that these observations of a uniquely labeled groundwater environment have significant implications relative to both past and future studies of speciation and transport in aqueous media. Aspects of these findings are relevant to the problems of waste disposal (both nuclear and non-nuclear) and to a variety of natural geochemical processes. Although improved sampling and characterization techniques are needed, existing methods can be used to further our understanding of environmental colloid behavior and transport.

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APPENDIX A: SAMPLE TREATMENT

Unless otherwise noted, all prefilters (nominal pore size $1.0\text{ }\mu\text{m}$) were felt bags and all $0.45\text{ }\mu\text{m}$ and $0.20\text{ }\mu\text{m}$ filters were hydrophilic terpolymer bag filters (Fin-L-Filter) supplied by Cole Parmer. The $0.05\text{ }\mu\text{m}$ filters were large flat filters of mixed cellulose acetate on cellulose nitrate composition supplied by Millipore. Samples were normally pumped through a manifold with the coarser filter in series and then through a filter holder that contained eight $0.05\text{ }\mu\text{m}$ filters in parallel.

Samples are listed in the order processed (filtered) rather than the order collected.

B-2: sampled 9 September 1983; volume pumped $5 \times 10^5\text{ l}$ ($1.3 \times 10^5\text{ gal}$); processed 12 December 1983. Filtered through $0.45\text{ }\mu\text{m}$ polycarbonate Nuclepore filters only; filter clogging and/or breakthrough believed to have occurred. Original sample volume 200 l; weight of evaporated $0.45\text{ }\mu\text{m}$ filtrate 63.8 g.

B-1: sampled 8 September 1983; volume pumped $2.1 \times 10^5\text{ l}$ ($5.6 \times 10^4\text{ gal}$); processed 27 July-15 August 1984. Filtered through prefilter, $0.45\text{ }\mu\text{m}$, $0.20\text{ }\mu\text{m}$; ultrafiltered through 100,000 MWU ($0.006\text{ }\mu\text{m}$) system. During ultrafiltration, the water not passing the ultrafilter was recycled through the entire filter string. Sample volume 188 l; retentate fluid volume 3.0 l; dried retentate weight 11.2 g; ultrafiltrate salt weight 48.1 g.

B-3: sampled 23 October 1984; $1.1 \times 10^7\text{ l}$ (volume pumped $3 \times 10^6\text{ gal}$); processed 1 February 1985. Filtered through prefilter, $0.45\text{ }\mu\text{m}$, $0.20\text{ }\mu\text{m}$. Sample volume 166 l, dried $0.2\text{ }\mu\text{m}$ filtrate weight 49.5 g.

B-4: sampled 23 October 1984; volume pumped $1.1 \times 10^7\text{ l}$ ($3 \times 10^6\text{ gal}$); processed 12-25 April 1985. Filtered through prefilter, $0.45\text{ }\mu\text{m}$, $0.20\text{ }\mu\text{m}$ and $0.05\text{ }\mu\text{m}$ filters in a single-pass operation; filtrate was then ultrafiltered (without recycling through filters) with a 10,000-MWU filter ($0.003\text{ }\mu\text{m}$). Two $0.45\text{ }\mu\text{m}$ bag filters were placed in series; the second filter collected approximately 50% as much activity as the first. Data from the two filters were added and reported as a single $0.45\text{ }\mu\text{m}$ value. Conventional filters were ashed for the first time (previously processed samples were subsequently retreated in the same way) and combined for recounting after being counted individually; difficulty was experienced with ashing the $0.05\text{ }\mu\text{m}$ filters, which reduced to a bead rather than a uniform ash. Sample volume 194.5 l; retentate volume 245 ml; dried retentate weight 2.04 g; ultrafiltrate salt weight 51.5 g.

B-5: sampled 28 May 1985; processed 13-20 August 1985. Sample collected $1.4 \times 10^7\text{ l}$ ($3.7 \times 10^6\text{ gal}$) from start of pumping, $1.1 \times 10^6\text{ l}$ ($2 \times 10^5\text{ gal}$) from restart of pumping at formation sampling point. Processing like B-4 except that only one $0.45\text{ }\mu\text{m}$ filter was used and the $0.05\text{ }\mu\text{m}$ filters were ashed before counting. Sample volume 184 l; retentate volume 328 ml; dried retentate weight 0.92 g; ultrafiltrate salt weight 39.8 g.

B-6: sampled 28 May 1985 (same pumped volumes as B-5); processed between 20 November 1985 and 14 January 1986. Processing same as B-5. Sample volume 200 l; retentate volume 350 ml; dried retentate weight 0.94 g; filtrate salt weight 43.7 g. Gamma counting of filters believed to have been compromised by use of ^{22}Na calibration source in counting room; ashed filter values used to determine total particulate ^{22}Na .

APPENDIX B: RADIONUCLIDE ANALYSES

Table B-1. Cheshire nuclide analysis for cavity sample B-1

Nuclide	Half life (a)	Total activity ($\mu\text{Ci/ml}$)*	Fraction of total activity retained by				Fraction dissolved
			Prefilter	0.45 μm	0.20 μm	0.006 μm	
^3H	12.26	0.615 (1)	na	na	na	na	1.000
^{22}Na	2.605	7.57×10^{-9} (24)	<0.001	0.061	<0.001	<0.06	0.939
^{40}K	1.3×10^9	2.67×10^{-9} (18)	<0.02	<0.02	<0.02	0.625	0.375
^{54}Mn	0.855	1.18×10^{-7} (25)	0.503	0.069	0.059	0.369	<0.14
^{60}Co	5.272	5.53×10^{-9} (16)	0.576	0.082	0.071	0.271	<0.004
^{106}Ru	1.020	1.25×10^{-5} (16)	0.189	0.084	0.067	0.578	0.082
^{125}Sb	2.760	5.27×10^{-6} (24)	0.007	0.003	0.002	0.039	0.949
^{134}Cs	2.065	2.18×10^{-8} (17)	0.055	0.020	0.016	0.322	0.587
^{137}Cs	30.170	3.19×10^{-6} (16)	0.084	0.024	0.016	0.326	0.550
^{144}Ce	0.778	1.20×10^{-8} (17)	0.280	0.074	0.055	0.591	<0.01
^{152}Eu	13.40	9.51×10^{-9} (17)	0.281	0.071	0.052	0.596	<0.01
^{154}Eu	8.50	1.64×10^{-8} (17)	0.286	0.073	0.053	0.588	<0.01
^{155}Eu	4.73	4.10×10^{-8} (16)	0.313	0.082	0.059	0.547	<0.01

* All activities decay-corrected to $T_0 = 14$ February 1976. Values in parentheses are the % uncertainties ($\pm 1 \sigma$) based on counting uncertainties for the individual samples:

na = not analyzed.

Table B-2. Cheshire nuclide analysis for cavity sample B-2

Nuclide	Half life (a)	Total activity ($\mu\text{Ci/ml}$)*	Fraction of total activity	
			retained on 0.45 μm	<0.45 μm
^3H	12.26	0.614 (1)	na	1.000
^{22}Na	2.605	9.79×10^{-9} (23)	0.079	0.921
^{40}K	1.3×10^9	5.24×10^{-9} (19)	0.269	0.731
^{54}Mn	0.855	1.20×10^{-7} (22)	0.341	0.659
^{60}Co	5.272	6.07×10^{-9} (18)	0.332	0.668
^{106}Ru	1.020	1.48×10^{-5} (21)	0.185	0.815
^{125}Sb	2.760	6.27×10^{-6} (25)	0.007	0.993
^{134}Cs	2.065	2.68×10^{-8} (21)	0.182	0.818
^{137}Cs	30.170	3.40×10^{-6} (20)	0.212	0.788
^{144}Ce	0.778	1.49×10^{-8} (20)	0.209	0.791
^{152}Eu	13.40	1.20×10^{-8} (21)	0.197	0.803
^{154}Eu	8.50	1.90×10^{-8} (21)	0.169	0.831
^{155}Eu	4.73	6.10×10^{-8} (21)	0.191	0.809

* All activities decay-corrected to $T_0 = 14$ February 1976. Values in parentheses are the % uncertainties ($\pm 1 \sigma$) based on counting uncertainties for the individual samples.

na = not analyzed.

Table B-3. Cheshire nuclide analysis for cavity sample B-3

Nuclide	Half life (a)	Total activity ($\mu\text{Ci/ml}$)*	Fraction of total activity retained by			Fraction of total activity $<0.20 \mu\text{m}$
			Prefilter	$0.45 \mu\text{m}$	$0.20 \mu\text{m}$	
^3H	12.26	0.504 (1)	na	na	na	1.000
^{22}Na	2.605	8.02×10^{-9} (25)	0.019	<0.008	<0.002	0.981
^{40}K	1.3×10^9	3.58×10^{-9} (24)	[combined filters, 0.03]			0.097
^{54}Mn	0.855	9.64×10^{-8} (64)	[combined filters, 0.128]			0.872
^{60}Co	5.272	3.42×10^{-9} (22)	0.068	0.035	0.031	0.866
^{106}Ru	1.020	1.14×10^{-5} (23)	0.029	0.029	0.025	0.917
^{125}Sb	2.760	6.77×10^{-6} (25)	0.001	0.002	0.001	0.996
^{134}Cs	2.065	2.70×10^{-8} (37)	0.008	nd	nd	0.992
^{137}Cs	30.170	4.60×10^{-6} (24)	0.009	0.007	0.008	0.976
^{144}Ce	0.778	1.01×10^{-8} (24)	0.051	<0.004	<0.003	0.949
^{152}Eu	13.40	7.52×10^{-9} (23)	0.047	0.024	0.027	0.902
^{154}Eu	8.50	1.31×10^{-8} (23)	0.044	0.025	0.026	0.905
^{155}Eu	4.73	3.87×10^{-8} (23)	0.044	0.022	0.023	0.911

* All activities decay-corrected to $T_0 = 14$ February 1976. Values in parentheses are the % uncertainties ($\pm 1 \sigma$) based on counting uncertainties for the individual samples.

na = not analyzed.

nd = not detected; no limit calculated.

Fraction dissolved

1.000
0.939
0.375
<0.14
<0.004
0.082
0.949
0.587
0.550
<0.01
<0.01
<0.01

σ based on

Table B-4. Cheshire nuclide analysis for cavity sample B-4

Nuclide	Half life (a)	Total activity ($\mu\text{Ci/ml}$)*	Fraction of total activity retained by					Fraction dissolved
			Prefilter	$0.45 \mu\text{m}$	$0.20 \mu\text{m}$	$0.05 \mu\text{m}$	$0.003 \mu\text{m}$	
^3H	12.26	0.504 (1)	na	na	na	na	na	1.000
^{22}Na	2.605	8.50×10^{-9} (23)	<0.18	<0.01	0.022	0.013	0.037	0.928
^{40}K	1.3×10^9	4.15×10^{-9} (20)	0.198	0.039	0.079	0.330	0.084	0.270
^{54}Mn	0.855	3.31×10^{-8} (36)	0.750	0.250	<0.14	<0.12	nd	nd
^{60}Co	5.272	3.12×10^{-9} (25)	0.368	0.129	0.155	0.123	0.204	0.021
^{106}Ru	1.020	1.05×10^{-5} (22)	0.321	0.129	0.158	0.070	0.178	0.144
^{125}Sb	2.760	7.30×10^{-6} (24)	0.006	0.005	0.004	0.003	0.014	0.968
^{134}Cs	2.065	2.67×10^{-8} (19)	0.111	0.038	0.048	0.067	0.057	0.679
^{137}Cs	30.170	4.39×10^{-6} (19)	0.116	0.041	0.055	0.068	0.075	0.645
^{144}Ce	0.778	9.56×10^{-9} (25)	0.362	0.132	0.140	0.071	0.295	<0.05
^{152}Eu	13.40	6.75×10^{-9} (25)	0.359	0.127	0.162	0.135	0.209	0.008
^{154}Eu	8.50	1.17×10^{-8} (25)	0.364	0.130	0.161	0.127	0.218	<0.01
^{155}Eu	4.73	3.45×10^{-8} (25)	0.345	0.118	0.148	0.109	0.280	<0.03

* All activities decay-corrected to $T_0 = 14$ February 1976. Values in parentheses are the % uncertainties ($\pm 1 \sigma$) based on counting uncertainties for the individual samples.

na = not analyzed.

nd = not detected; no limit calculated.

Table B-5. Cheshire nuclide analysis for formation sample B-5

Nuclide	Half life (a)	Total activity ($\mu\text{Ci/ml}$)*	Fraction of total activity retained by					Fraction dissolved
			Prefilter	0.45 μm	0.20 μm	0.05 μm	0.003 μm	
^3H	12.26	0.433 (1)	na	na	na	na	na	1.000
^{22}Na	2.605	1.07×10^{-9} (24)	<0.02	<0.02	0.057	<0.28	<0.20	0.943
^{40}K	1.3×10^9	2.94×10^{-9} (20)	0.047	<0.01	<0.01	0.118	0.083	0.752
^{54}Mn	0.855	7×10^{-9} (72)		[combined filters, 1.0]				<0.01
^{60}Co	5.272	1.06×10^{-10} (25)	0.441	<0.05	0.097	0.294	0.168	<0.04
^{106}Ru	1.020	2.67×10^{-6} (20)	0.162	0.071	0.055	0.289	0.205	0.217
^{125}Sb	2.760	3.93×10^{-6} (25)	0.003	0.002	0.004	0.004	0.006	0.985
^{134}Cs	2.065	1.91×10^{-9} (25)	nd	nd	nd	nd	0.024	0.976
^{137}Cs	30.170	7.43×10^{-7} (22)	0.018	0.005	0.007	0.050	0.035	0.884
^{144}Ce	0.778	$<7.5 \times 10^{-11}$	nd	nd	nd	nd	nd	nd
^{152}Eu	13.40	1.65×10^{-10} (25)	0.237	<0.07	<0.08	0.458	0.305	<0.06
^{154}Eu	8.50	2.99×10^{-10} (25)	0.245	<0.02	<0.02	0.466	0.289	<0.07
^{155}Eu	4.73	8.80×10^{-10} (25)	0.173	0.034	0.066	0.382	0.345	<0.13

* All activities decay-corrected to $T_0 = 14$ February 1976. Values in parentheses are the % uncertainties ($\pm 1 \sigma$) based on counting uncertainties for the individual samples.

na = not analyzed.

nd = not detected; no limit calculated.

Table B-6. Cheshire nuclide analysis for formation sample B-6

Nuclide	Half life (a)	Total activity ($\mu\text{Ci/ml}$)*	Fraction of total activity retained by					Fraction dissolved
			Prefilter	0.45 μm	0.20 μm	0.05 μm	0.003 μm	
^3H	12.26	0.433 (1)	na	na	na	na	na	1.000
^{22}Na	2.605	1.49×10^{-9} (19)		[combined filters, <1.0]			<0.01	>0.99
^{40}K	1.3×10^9	2.79×10^{-9} (21)	0.036	<0.01	<0.01	0.094	0.020	0.850
^{54}Mn	0.855	$<6 \times 10^{-9}$	nd	nd	nd	nd	nd	nd
^{60}Co	5.272	5.30×10^{-11} (25)	1.000	<0.10	<0.10	<0.10	<0.05	<0.09
^{106}Ru	1.020	1.79×10^{-6} (12)	0.292	0.084	0.039	0.217	0.053	0.315
^{125}Sb	2.760	3.98×10^{-6} (25)	0.003	0.001	0.001	0.002	0.002	0.991
^{134}Cs	2.065	3.52×10^{-10} (25)	nd	nd	nd	nd	nd	>0.90
^{137}Cs	30.170	5.46×10^{-7} (23)	0.029	0.007	0.005	0.044	0.010	0.905
^{144}Ce	0.778	$<9 \times 10^{-11}$	nd	nd	nd	nd	nd	nd
^{152}Eu	13.40	8.98×10^{-11} (16)	0.404	<0.10	<0.10	0.492	0.104	<0.24
^{154}Eu	8.50	1.92×10^{-10} (15)	0.453	0.120	<0.02	0.342	0.085	<0.12
^{155}Eu	4.73	5.24×10^{-10} (16)	0.367	<0.04	<0.03	0.537	0.096	<0.39

* All activities decay-corrected to $T_0 = 14$ February 1976. Values in parentheses are the % uncertainties ($\pm 1 \sigma$) based on counting uncertainties for the individual samples.

na = not analyzed.

nd = not detected; no limit calculated.



ENVIRONMENTAL RESEARCH BRIEF

Colloidal-Facilitated Transport of Inorganic Contaminants in Ground Water: Part I. Sampling Considerations

Robert W. Puls^a, James H. Eychaner^b, and Robert M. Powell^c

Abstract

Investigations at Pinal Creek, Arizona, evaluated routine sampling procedures for determination of aqueous inorganic geochemistry and assessment of contaminant transport by colloidal mobility. Sampling variables included pump type and flow rate, collection under air or nitrogen, and filter pore diameter. During well purging and sample collection, suspended particle size and number as well as dissolved oxygen, temperature, specific conductance, pH, and redox potential were monitored. Laboratory analyses of both unfiltered samples and the filtrates were performed by inductively coupled argon plasma, atomic absorption with graphite furnace, and ion chromatography. Scanning electron microscopy with Energy Dispersive X-ray was also used for analysis of the filtered particulates.

Suspended particle counts consistently required approximately twice as long as the other field-monitored indicators to stabilize. High-flow-rate pumps entrained normally nonmobile particles. Differences in elemental concentrations using different filter-pore sizes were generally not large with only two wells having differences greater than 10 percent in most elemental concentrations, although trends showed increasing concentrations with increasing filter pore sizes in most wells. Similar differences (> 10%) were observed for some wells when samples were collected under nitrogen rather than in air. $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios for air-collected samples were smaller than for samples

collected under a nitrogen atmosphere, reflecting sampling-induced oxidation.

Introduction

Ground-water samples that are representative of actual ground-water quality are, at best, difficult to obtain (Claassen, 1982). Disturbance of the subsurface environment is unavoidable during well construction activities. Additional disturbance during sample collection may drastically alter ground-water chemistry due to oxidation, sorption, mixing, and turbulent flow resulting in inaccurate estimations of contaminant loading and transport predictions. A common study objective is to determine what constituents are mobile in an aquifer. Many ground-water samples are filtered to exclude particles dislodged from the local well environment, because those particles are not mobile at ordinary ground-water velocities. Because geochemical models are based on the thermodynamics of dissolved constituents, small pore-diameter filters have been preferred as the best way to separate dissolved from particulate constituents.

In practice, 0.45- μm filters are commonly used to balance between the objectives of isolating dissolved constituents and permitting reasonable use in the field. Unfortunately, particle sizes do not have an express lower bound so that the right filter can perfectly separate particles from solutes. Particles with diameters from 0.003 to 10 μm , referred to as colloids, may form in certain environments and be mobile at ground-water velocities. Use of 0.45- μm filtration may exclude an important component of the contaminant load at some waste sites, particularly where highly toxic metals are involved (Puls and Barcelona, 1989).

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Many studies have demonstrated contaminant transport by colloidal mobility (Gschwend and Reynolds, 1987; Eichholz et al. 1982; Enfield and Bengtsson, 1988; Robertson, 1984). There is increasing concern that current methods of ground-water sample collection may exclude this component of the contaminant loading in a given system. If the purpose of sampling is to estimate contaminant transport, substantial underestimations of mobility may result, because of colloidal associations. Numerous studies attest to the strong sorptive capabilities of secondary clay minerals; hydrous Fe, Al, and Mn oxides; and humic material of colloidal dimensions. Takayanagi and Wong (1984) determined that more than 70 percent of the total Se in river waters adjacent to the Chesapeake Bay was associated with organic and inorganic colloidal particles. Buddemeier and Rego (1986) found that virtually all the activity of Mn, Co, Sb, Cs, Ce, and Eu was associated with colloidal particles in ground-water samples from underground nuclear-test cavities at the Nevada Test Site. Colloidal particles generated in batch experiments by Sheppard et al. (1979) and Puls et al. (1989) were shown to retain substantial proportions of radionuclides. Further work by Sheppard et al. (1980) concluded that the transport of radionuclides by colloidal clay particles should be considered in contaminant-transport models.

Filtration is part of this concern; but other factors, such as sample exposure to atmospheres different from aquifer environments and pump-induced disturbance of the sampling zone, are also important. Oxidation-induced precipitation and sorption processes, many of which are kinetically rapid (seconds to minutes), may cause previously dissolved species to be removed during filtration, resulting in lower metal concentrations than are actually present in the aquifer. Filter loading and clogging with fine particles may also occur, reducing the nominal pore size of the filter and introducing errors due to changing effective pore size (Danielsson, 1982).

Background

A workshop was convened at the Robert S. Kerr Environmental Research Laboratory (RSKERL) of the U.S. Environmental Protection Agency in 1988 to examine these issues and provide technical guidance based on currently available scientific information. A Superfund Ground Water Issue Paper resulting from the workshop emphasized the importance of well construction and sampling methodology in obtaining representative water chemistry data (Puls and Barcelona, 1989). Workshop recommendations in the area of ground-water sampling are briefly summarized below:

Purging

Water that remains in the well casing between sampling periods is unrepresentative of water in the formation opposite the screened interval. It must be removed by purging or isolated from the collected sample by a packer arrangement prior to the collection of representative water samples. It is important to purge the stagnant water at flow rates below those used in development to avoid further development, well damage or the disturbance of accumulated corrosion or reaction products in the well.

Isolation of Sampling Zone

Isolation of the sampling zone is necessary to minimize the purge volume as well as to minimize air contact. This is

especially important since Eh/pH conditions of the formation waters are often sensitive to dissolved-gas content. Inflatable packers can be used to achieve isolation of the sampling zone.

Pumping for Sample Collection

It is recommended that a positive displacement pump be used. Other types of sample collection (e.g. bailing) may cause displacement of non-mobile particles or substantially alter ground-water chemistry leading to colloid formation (e.g. vacuum pumps). Surging must be avoided, and a flow rate close to the actual ground-water flow rate should be employed. While an initial approximation, flow rates around 100 to 500 ml/min have been used to successfully sample ground waters in a quiescent mode.

Assessment of Water Constituents During Purging and Sampling

Monitoring for dissolved oxygen, temperature, specific conductance, pH and turbidity during purging and sampling is recommended to determine baseline ground-water quality conditions prior to sampling.

Filtration

For estimates of contaminant mobility, filtration with coarse filters ($\geq 2 \mu\text{m}$) using the same procedures as above or collection of unfiltered samples is recommended. Filtration for accurate estimations of geochemistry should be performed in the field with in-line pressure filtration using a large (e.g. 142 mm) polycarbonate-type (thin with sharp pore-size cutoff) 0.1 μm filter. Air contact should be minimized and entirely excluded for some samples. Acidification of samples to $< \text{pH } 2$ should be performed immediately. The filter holder should be non-metallic. Holders made of steel are subject to corrosion and may introduce non-formation metals into samples. Prewashing of filters should be routinely performed.

In an effort to test the efficacy of these recommendations, a joint study by the U.S. Environmental Protection Agency and the U.S. Geological Survey was begun in the spring of 1988. Collection of representative unfiltered samples is quite challenging in many systems because of the difficulty of excluding nonsuspended or artifact particulates. Because no sampling technique is totally passive, all contaminant-mobility estimates based on unfiltered samples are biased toward overestimation. An attempt was made to minimize this bias by carefully following the workshop recommendations.

Purpose and Objectives

The specific objectives of the study were to evaluate perturbations to the ground-water geochemistry during sample collection and, in particular, to identify those factors that caused significant differences in elemental concentrations or concentrations and size distributions of suspended particles in samples collected for analysis. Samples for both dissolved and suspended contaminants were collected. Filters smaller than 0.45 μm were used to sample for dissolved constituents and for comparison with the unfiltered or coarsely filtered samples. This document summarizes the results of the study and addresses the efficacy of the 1988 RSKERL filtration workshop recommendations on ground-water sampling for metals analyses.

Study Site

The study site is located at Pinal Creek, near Globe, Arizona, about 130 km east of Phoenix and about 170 km north of Tucson. Copper has been mined since 1903 from granite porphyry adjacent to an aquifer at the site. A band of unconsolidated alluvium 300 to 800 m wide, as much as 50 m thick, and about 20 km long forms the upper, central part of the aquifer in a valley along Miami Wash and Pinal Creek (Figures 1 and 2). Most of the sediment in the alluvium ranges in size from fine sand to coarse gravel, but clay and boulder lenses also are present. Alluvial basin fill more than 100 m thick forms the remainder of the aquifer beneath and adjacent to the unconsolidated alluvium. Peterson (1962) described the geology of the area.

During 1940-86, acidic mining waste solutions were discarded in an unlined lake formed behind waste and tailings piles. In 1986, pH at the lake surface was about 2.7 and the lake volume was about $5.5 \times 10^6 \text{ m}^3$. By May 1988, virtually all the lake water had been spread on inactive tailings piles to evaporate. Contamination of ground and surface waters in the area has been described by Eychaner (1989). The distribution of pH in the aquifer was used as a guide in selecting wells to sample for this study (Figure 1).

Water levels and chemical quality have been monitored since 1984 in several groups of observation wells (Figure 1). Each group consists of separate wells individually completed with 10-cm-diameter polyvinylchloride casing and a single well screen. Most of the well screens are 0.9 m long; the longest screen in a

well sampled for this study is 6.1 m. Most of the wells were drilled by the hydraulic rotary method using bentonite-based drilling mud; five wells were drilled by the hollow-stem auger method. The annulus in the screened interval was packed with washed pea gravel from a nearby uncontaminated area. The gravel pack was capped with a 1-m layer of bentonite pellets. Each well was developed by jetting high-pressure air through the screen to dislodge and remove fine-grained material. Comprehensive data from the study area are available (Eychaner et al, 1989).

In the alluvium, hydraulic conductivity is on the order of 200 m/d on the basis of cross-sectional area, hydraulic gradient, and measured outflow (C.C. Neaville, hydrologist, U.S. Geological Survey, written commun., 1990). For thick sections of basin fill, hydraulic conductivity was estimated from aquifer tests of two wells to range from 0.1 to 0.2 m/d (Neaville, written commun., 1990).

Near the sampled wells, hydraulic conductivity was estimated on the basis of measured water-level declines and pumping rates during sampling periods using the solution of the unsteady ground-water flow equation (Lohman, 1979, eq. 44). The estimates are within an order of magnitude at best, but are useful for comparisons among the wells because of the similarities in construction. The estimates range from 10 to 150 m/d for wells in the alluvium or uppermost basin fill. Estimated hydraulic conductivity for well 105, deeper in the basin fill, was 0.5 m/d. On the basis of hydraulic gradients that range from 0.005 to 0.008 and assumed porosity of 0.2 or 0.3, average ground-water flow velocities near the wells range from 0.02 to 3 m/d.

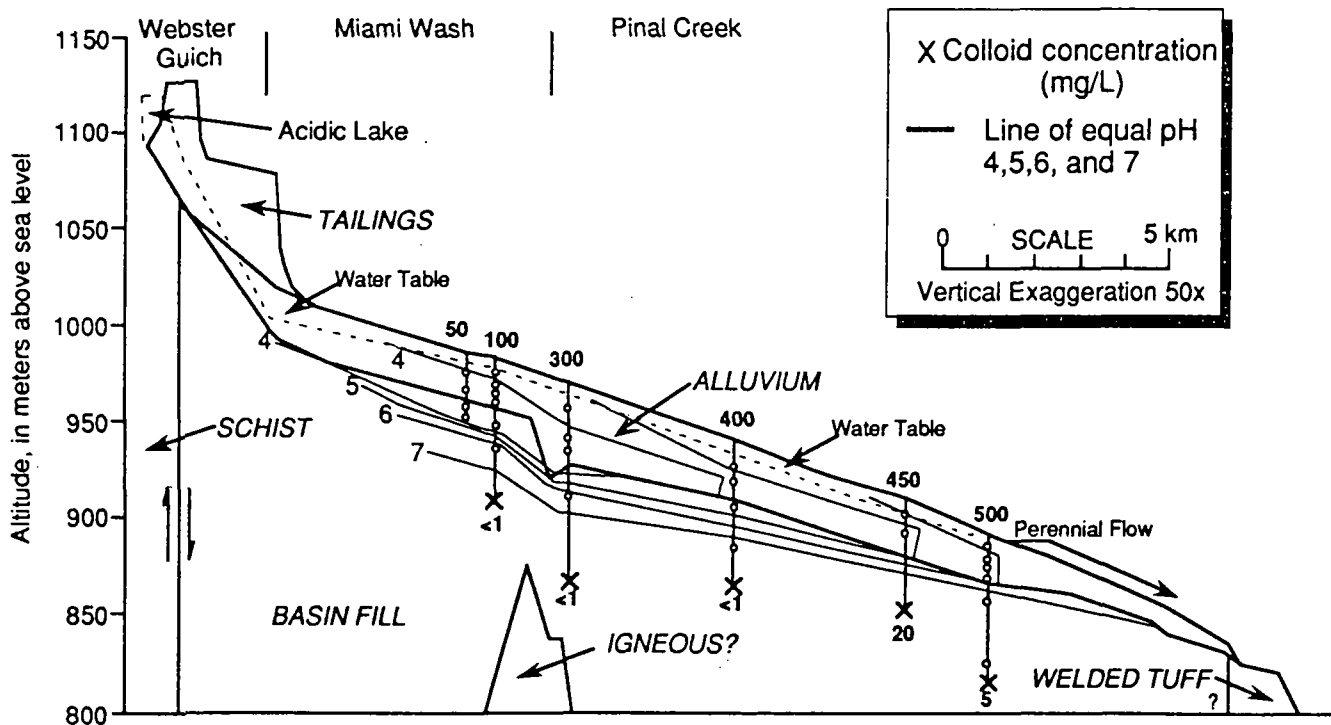


Figure 1. Hydrogeologic Section of the Aquifer

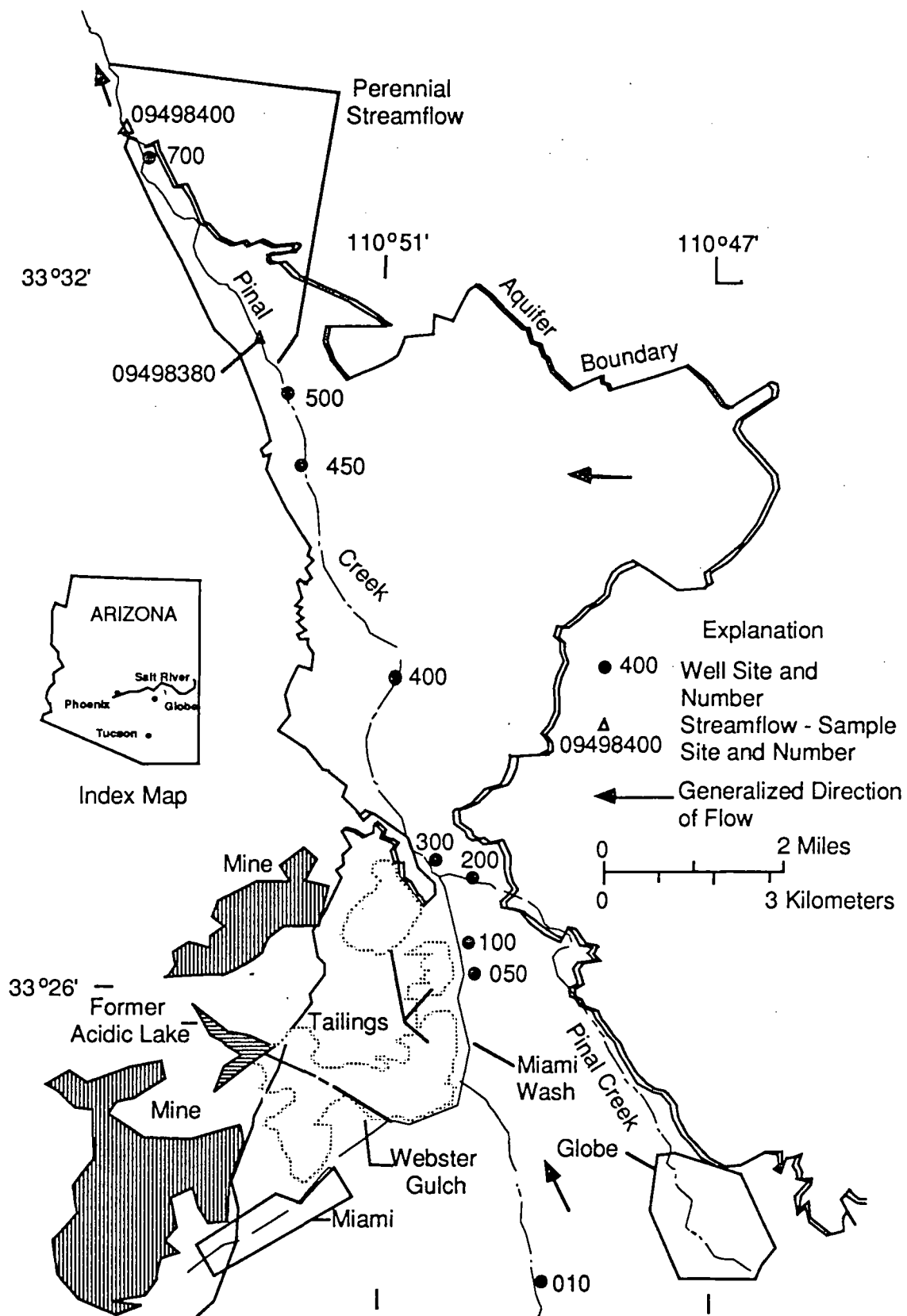


Figure 2. Plan-View of Study Site

Instrumentation and Methods

Ground water was collected during two field seasons from twelve wells selected to represent the range of pH, solute concentration, and hydraulic conductivity along Pinal Creek (Figures 1 and 2). Three different pumps were used (Table 1). At the lowest discharge, velocities induced at the borehole face were estimated to range from 1 to 5 times the average ground-water velocity close to each well in the alluvium. In the basin fill underlying the alluvium, even the lowest discharge resulted in velocities more than 400 times that of the ground water.

Water that remained in the well between sampling sessions was purged, as it was judged to be unrepresentative of formation water. An inflatable packer was used with the bladder and low-rate submersible pumps to reduce necessary purge volumes. During purging, a Hydrolab Surveyor II¹ with a flow-through cell was used to monitor temperature, specific conductance, pH, dissolved oxygen, and oxidation-reduction potential (Pt electrode). Samples were collected only after each indicator reached an acceptably stable value, generally a value that changed by less than its measurement uncertainty during one purge volume. From 3 to 24 volumes were purged before sampling, and the high flow rate submersible pump generally purged the larger volumes.

During the second field season, a Malvern Autosizer IIc was used to measure suspended particles in the diameter range from 0.003 to 3 μm . The instrument determines the size distribution of suspended particles in this size range using laser light scattering techniques together with photon correlation spectroscopy. Particle-concentration estimates were based on calibration curves constructed using linear correlation ($r^2 = 0.999$) between photon counts by the instrument and known concentrations of kaolinite, a secondary clay mineral. The kaolinite used was a reference standard obtained from the Clay Minerals Repository at the University of Missouri. Kaolinite was identified by Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) on many of the filters from the sampled wells. Other particles captured on filters and identified by SEM-EDX included iron oxides, smectite, jarosite, silica, and gypsum. Although the assumption that minerals in the reference

standard adequately represent the sum total of all the colloids in the aquifer is not entirely true, photon counts provide at least a relative measure of suspended particle concentrations.

Colloid concentrations took longer to stabilize than other field indicators, about 50 percent longer than dissolved oxygen or redox potential, and about twice as long as specific conductance, pH, or temperature. Well 107 was representative of the variation of the indicators during purging at most of the wells (Figure 3). Stable values of the indicators at selected wells are listed in Table 2.

Samples were collected both in air and under nitrogen using a field glove box. Unfiltered and filtered samples were collected, the latter using 142-mm-diameter Millipore and Nucleopore membrane filters ranging in pore size from 0.03 to 10.0 μm . Samples were acidified in the field immediately after filtering with double distilled concentrated nitric acid to pH < 2. Working in the glove box was difficult, and handling thin membrane filters with latex gloves was particularly cumbersome.

Elemental analyses were performed with inductively coupled plasma (ICP) for most elements; atomic absorption with graphite furnace (AAGF) for Cd, Pb, and As; and ion chromatography (IC) for chloride and sulfate. Analytical precision on the ICP and AAGF were $\leq \pm 10$ percent, and on the IC $\leq \pm 5$ percent. Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) was used to identify colloidal material captured on the membrane filters.

Effects of Sampling Variables

Pumping Rates

Differences in pumping rates were expected to cause differences in the concentrations and size distributions of colloidal particles in suspensions and differences in elemental concentrations after filtration. Ten wells were purged and sampled with as many as three different types of pumps in June 1988 and March 1989. Pumping rates ranged from 0.6 to 92 L/min, corresponding to velocities of 25 to 3900 m/d at the well screens. Samples were filtered in air through 0.4- μm filters, filtrates were analyzed for

Table 1. Pumps used in ground water sampling.

Brand ¹	Type	Power Supply	Diameter (mm)	Discharge (L/min)
GeoTech	bladder	compressed air	44	0.6 - 1.1
Keck	submersible	12 V dc	44	2.8 - 3.8
Grundfos	submersible	240 V ac	95	12 - 92

¹ Use of brand names is for identification purposes only and does not imply endorsement by any agency of the United States Government.

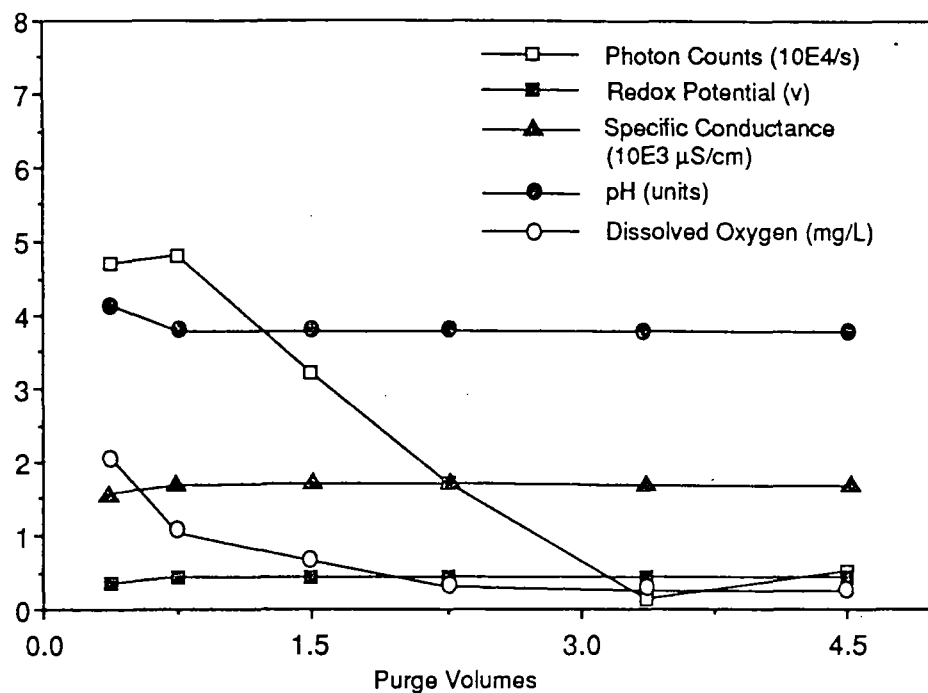


Figure 3. Changes in Water Quality Indicators During Purging of Well 107 (Keck Pump, 3/89)

Table 2. Ground-water quality indicators for selected wells.

Well:	104	105	107	303	403	451	503
pH (units)	3.92	6.08	3.48	4.27	5.05	4.73	5.74
Sp.Cond.(μS/cm)	3020	4300	7070	3210	3200	4060	3620
Temp.(°C)	18.0	19.0	18.4	19.0	18.8	18.9	18.9
Oxygen(mg/L)	0.39	—	0.14	0.01	0.07	0.24	0.22
Redox Pot.(v)	0.44	0.28	0.44	0.37	0.38	0.25	0.32
Colloids (mg/L)	—	0.4	0.3	—	—	20	0.1

cations using ICP, and the filters were examined using SEM-EDX. Particle concentrations and size distributions were monitored in 1989 for five wells on unfiltered samples.

Cation concentrations differed by less than 10 percent between pumping rates for seven of the ten wells. These seven wells generally had low particle counts, and low filter loading was observed using SEM-EDX. Well 503, in the alluvium, was representative of the seven wells. Figure 4 illustrates changes in water-quality indicators in well 503, where the bladder pump was used to purge and sample, followed by use of the low-rate and high-rate submersible pumps. The well therefore was purged with the bladder pump prior to placement of the latter two pumps. Colloid concentration stabilized at 0.1 mg/L during pumping at 1.1 L/min and increased to 0.7 mg/L when discharge increased to 3.8 L/min before stabilizing again at 0.1 mg/L. When discharge increased to 30 L/min, however, colloid concentration initially increased to 4.4 mg/L before finally stabilizing at 0.2 mg/L. Particle-size distributions for the final sample with each pump are also shown in Figure 4. The low-discharge pumps produced monomodal distributions of the same size particles. The highest discharge produced larger and slightly more particles in a bimodal distribution because of increased turbulence. The predominant mineral identified on the filters from well 503 was gypsum, which was accompanied by some iron oxide, kaolinite, and other particles that contained Fe+Al+S. Analytical concentrations of metals did not differ significantly but did reflect the observed mineralogy.

For samples from the three wells where observed cation differences exceeded 10 percent, measured particle counts and filter loading were also significantly higher than for the other

seven wells. Particle counts differed by factors of 5 to 130 between pumping rates. Cation concentrations differed by as much as 50 percent for both major and trace elements. Cation concentrations were generally highest in samples with the lowest counts (least turbid), but some anomalous behavior was observed for some elements (Table 3). Pump-induced entrainment of colloidal particles could decrease dissolved cation concentrations by sorption on freshly exposed surfaces of particles which had been retained on filters.

Differences in cation concentrations were especially noticeable at well 105. In March 1989, pumping at 2.8 L/min mobilized 13 times more particles and decreased Ca, Mg, Mn, and Sr concentrations by 10 to 25 percent, compared to pumping at 0.9 L/min (Table 3). For equal volumes of filtrate, SEM photographs showed that the proportion of the area of a 0.1 μ m filter covered with particles was about 1 percent for the lower pumping rate and about 30 percent for the higher rate. In June 1988, pumping at 12 L/min decreased concentrations of Ca, Mg, Mn, Co, Ni, and Sr by 20 to 50 percent compared to pumping at 1 L/min. Well 105 is screened in the basin fill, which has the lowest ground-water flow velocity in this study. Even at the lowest pumping rate, the velocity induced at the borehole face was more than 400 times the normal ground-water velocity. Water pumped from well 105 was visibly murky at times.

Pumping well 451 at 0.8 L/min produced seven times more particles than pumping at 3.4 L/min and decreased concentrations of six cations by 10 to 50 percent. Again, the less turbid water generally had the larger concentrations, but the higher pumping rate unexpectedly produced the less turbid water. This well had the highest colloid concentrations of any well (Table 4). The

Table 3. Cation and colloid concentrations, mg/L, after purging at different rates (March 1989, 0.4 μ m filter, sampled in air).

Well	105	105	451	451	503	503	503
Discharge (L/min)	0.9	2.8	0.8	3.4	1.1	3.8	30
Colloids	0.3	4.0	20	3.0	0.1	0.1	0.2
Ca	579	478	586	623	703	704	704
Mg	149	117	150	162	148	146	147
K	40	37	16	13	12	11	11
Fe	<.4	<.4	156	151	<.4	<.4	<.4
Mn	6.6	5.0	108	113	76	76	73
Al	<.4	<.4	6.5	10.0	<.4	<.4	<.4
Cu	<.4	<.4	6.4	12.4	<.4	<.4	<.4
Co	<.4	<.4	1.5	1.8	<.4	<.4	<.4
Ni	<.4	<.4	0.3	0.4	0.6	0.6	0.6
Sr	1.6	1.4	1.9	2.1	2.3	2.3	2.3
Zn	0.7	0.9	3.0	3.9	0.06	0.04	0.04

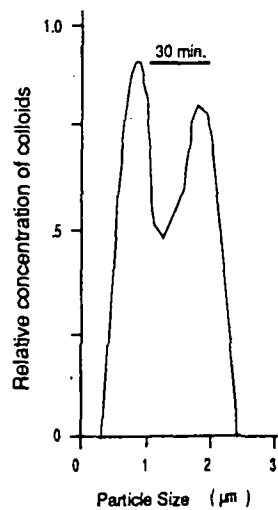
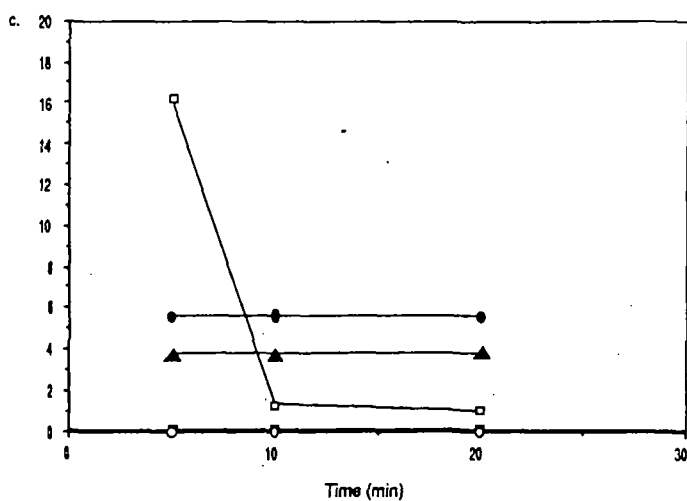
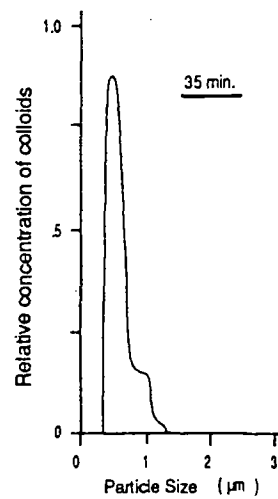
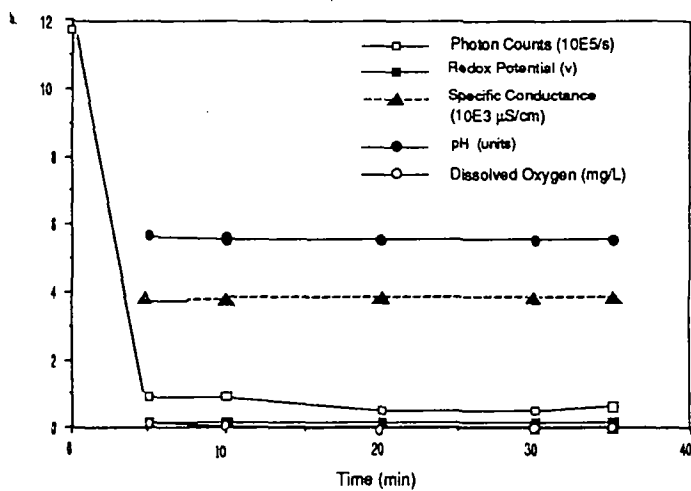
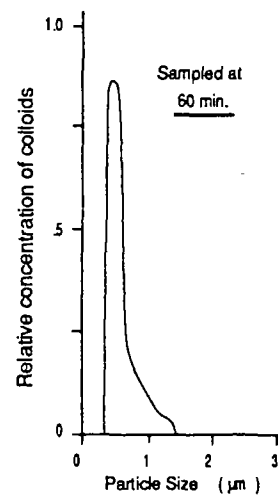
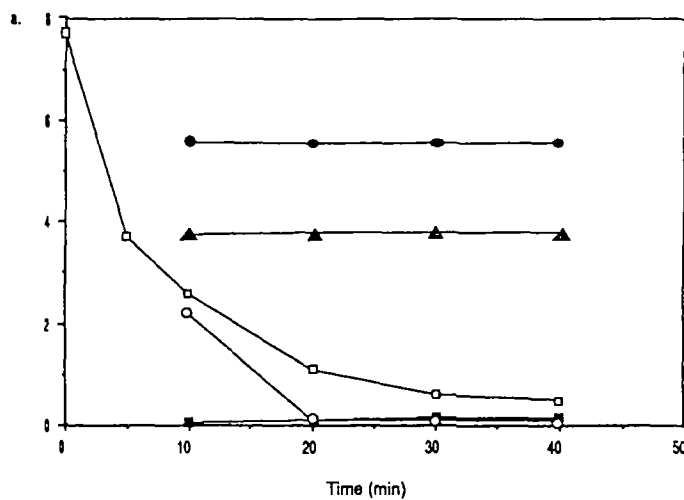


Figure 4a-c. Changes in Water Quality Indicators During Purging of Well 503: (a) Bladder Pump; (b) Low Speed Submersible Pump; (c) High Speed Submersible Pump

Table 4. Pumping rate data for selected wells and pumps.

Well	Date Sampled	Pump Discharge (L/min)	Intake Velocity (m/d)	Formation Velocity (m/d)	Relative Velocity ²	Colloid Concentration (mg/L)
105	6-14-88	1.0	42	0.012	460	0.3
		12	510		5500	
	3-7-89	0.9	38		410	
303	6-15-88	2.8	120	1.33	1300	4.0
		0.7	30		2.9	
		24	1000		99	
403	6-15-88	0.8	34	2.93	1.5	
		27	1100		51	
451	3-9-89	0.8	26	0.25	5.3	20
		3.4	110		22	
452	3-9-89	0.8	28	0.75	1.8	0.2
		28	980		61	
503	6-16-88	1.0	42	1.63	3.4	0.1
		45	1900		150	
	3-8-89	1.1	47		3.7	
		3.8	160		13	
		30	1300		100	

² Ratio of induced velocity at the borehole face to average ground-water velocity in the adjacent formation.

samples collected in March 1989 were noticeably turbid, even after 2 hours of purging with the bladder pump. In fact, lower particle counts by the slightly higher rate pump may have resulted from the additional purge time, as the latter was inserted following purging and sampling with the bladder pump. Two factors may contribute to the high colloid concentrations at well 451:

- it is in relatively fine grained sediment in the alluvium, and
- it is in a part of the aquifer where pH is changing rapidly and iron oxide coatings on colloidal clay are dissolving.

For this data set, particle concentrations were not predictable from pumping rate, purge volume, flow velocity at the screen, or the ratio of velocity induced at the borehole face to local ground-water flow velocity. Measured particle concentrations appear to depend on interactions of these factors as well as geology, well construction, and water chemistry.

Filtration Differences

Concentration differences among samples filtered through pore sizes ranging from 0.1 to 10 μ m were generally less than 10 percent. Only wells 303 (Table 5) and well 503 had differences of greater than 10 percent in most elemental concentrations. The larger differences commonly were associated with use of the high-rate submersible pump, and concentrations generally increased with increasing filter-pore size.

Differences less than 10 percent generally were observed for waters that have pH less than 4, which does not favor colloid formation. The largest observed differences for well 403, for

Table 5. Cation concentrations, in mg/L, for well 303 using different filters (June 1988, 24 L/min, sampled in air).

Element	0.1 μ m	0.4 μ m	10 μ m
Ca	391	424	492
Mg	91	100	20
K	4.73	5.49	9.76
Fe	171	87	211
Mn	37.7	40.8	45.5
Al	6.74	7.61	9.93
Co	0.68	0.75	0.86
Cu	15.0	16.7	19.2
Ni	0.68	0.75	0.88
Zn	2.75	3.27	4.13

example, were for Al, Cu, Fe, and Mg, but no consistent trend of concentration with filter pore size is apparent (Table 6).

Filtration differences of greater than 10 percent were also generally associated with use of the high-rate submersible pump because of the increased entrainment of particulates as observed above.

Table 6. Cation concentrations, in mg/L, for well 403 using different filters (June 1988, 0.8 L/min, sampled in air).

Element	0.1 μ m	0.4 μ m	10 μ m
Ca	533	533	554
Mg	133	113	116
K	5.58	5.47	5.65
Fe	0.45	6.63	1.22
Mn	34.6	34.9	34.7
Al	1.22	1.91	1.17
Co	0.36	0.36	0.37
Cu	1.62	2.14	1.57
Ni	0.41	0.42	0.44
Zn	0.90	0.95	1.60

Oxidation of Samples

Oxidation of samples during sample collection, filtration, and preservation generally resulted in substantial differences in most wells between samples collected under nitrogen or in air. Work by Holm et al. (1988) showed that diffusion of atmospheric gases through pump tubing can introduce measurable concentrations of oxygen into waters initially low in dissolved oxygen. This source of possible contamination for both sets of samples was minimized by collection of samples adjacent to the wellhead. Samples collected in air were directly exposed to atmospheric gases during filtration and acidification procedures. Significant differences (>10 percent) were observed in many of the wells. Variations in differences from well to well may have been caused by a number of different factors including:

- slightly different exposure times to air, depending on water-table depth and duration of filtration and preservation,
- dissolved-oxygen level,
- redox potential (Eh), and
- dissolved iron concentration.

Large differences in concentrations were measured for well 303, where dissolved iron concentration was greater than 200 mg/L (Table 7). Differences similar to those for well 303 were also observed in wells 51, 104, and 403. In contrast, the differences were small for well 503, where the dissolved iron concentration was less than 0.1 mg/L.

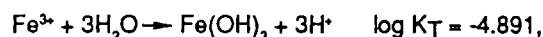
Another indication of the extent of oxidative effects on sample integrity was reflected in Eh values determined by various methods for well 51 (Figure 1). The field-measured Eh value using a Pt electrode was 0.43 V. A calculated Eh value, assuming equilibrium between Fe^{3+} and $\text{Fe}(\text{OH})_3$, was 0.57 V (Stollenwerk and Eychaner, 1989). In March 1989, Fe^{3+} and Fe_{total} for well 51

Table 7. Cation concentrations, in mg/L, for samples collected in air and nitrogen under atmosphere (mg/L, 0.40- μ m filter, < 1 L/min).

Element	Well 303		Well 503	
	air	nitrogen	air	nitrogen
Fe	177	215	0.04	0.09
Mn	37.4	44.7	68.3	68.7
Cd	0.02	0.02	0.01	0.01
Co	0.69	0.82	0.01	0.02
Cu	15.5	18.6	0.01	0.04
Ni	0.70	0.84	0.47	0.48
Zn	2.53	3.11	0.21	0.30

were determined within one week of sample collection; Fe^{3+} was computed by difference, and Eh was calculated from the ratio of Fe^{3+} to Fe^{2+} . The calculated Eh was 0.51 V for the sample collected and analyzed in a nitrogen atmosphere and 0.76 V for the sample collected in air. Samples collected in the glove box were transported in nitrogen-pressurized containers, and the determinations were performed in laboratory glove boxes also pressurized with nitrogen.

Several possible errors are associated with all these Eh evaluation methods. Lindberg and Runnells (1984) showed that many field Eh measurements may not reflect true redox conditions in ground waters. However, in acidic waters such as these, field measurements using Pt electrodes may be valid (Nordstrom et al. 1979). Values calculated from equilibrium constants rely on the assumption that $\text{Fe}(\text{OH})_3$ is the predominant solubility controlling phase. Stollenwerk and Eychaner (1989) used the equilibrium expression:



although other values have been reported for this reaction. Samples collected under nitrogen may have received some exposure to oxygen during sample collection, processing, and analysis. The Fe^{3+} values for March 1989 were small differences between two large numbers and are uncertain. Irrespective of these and other limitations in estimating Eh, the large difference observed between 0.76 V for the sample collected in air and the other Eh values for well 51 demonstrates the extent of oxidation that can occur if care is not taken to limit oxygen exposure during sample-collection activities in suboxic and anoxic environments.

Conclusions

Research at this site indicates that monitoring of water-quality indicators during well purging and sampling is important. In addition to the indicators most often monitored, turbidity also needs to be evaluated before collecting samples. In lieu of the use of a turbidimeter, purging for twice the time required for dissolved-oxygen equilibration may be a good rule of thumb.

The use of a low flow rate pump can minimize entrainment of nonmobile suspended particulates, oxygenation of formation water, and mixing of adjacent, possibly geochemically distinct, ground waters. Collection and processing of anoxic or suboxic ground water excluding atmospheric gases to the extent possible is desirable for representative and accurate water-chemistry data. The glove box used for collection of samples under nitrogen was cumbersome and difficult to use, especially in handling the thin membrane filters. If tubing of minimum length and maximum thickness were used, in-line filtration would probably mitigate the oxidation effects observed in the present study, making the use of a field glove box and accompanying nitrogen cylinders unnecessary. Although filtration differences generally were not significant at this site, trends indicate that care needs to be taken in selection of filter pore size and that samples need to be filtered in the field. Additional research is needed at sites with distinctly different hydrology, geology, and chemistry before final recommendations can be made concerning filtration. In the interim, collection of filtered and unfiltered samples for comparison purposes is suggested for at least a fraction of the samples collected. Filtered samples are needed for accurate aqueous geochemistry estimations, and unfiltered samples provide conservative estimates of contaminant mobility.

The sampling recommendations proposed by the RSKERL 1988 workshop participants were realistic and relatively easy to apply in the present study. Additional time was required for purging and sampling, but the additional care was warranted to obtain groundwater chemistry data which were as representative as possible.

Disclaimer

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MECHANISMS RESTRICTING CONTAMINANT TRANSPORT IN A
SHALLOW, TRANSMISSIVE GROUNDWATER SYSTEM
IN SOUTH FLORIDA

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ABSTRACT

Contaminated soils underlying the Petroleum Products Corporation National Priority List site in Broward County, Florida, exhibit lead and petroleum hydrocarbon concentrations exceeding 20,000 and 100,000 ppm, respectively. In contrast, chromium concentrations never exceed 100 ppm. Despite this difference in soil load, all three shallow groundwater contaminant plumes encompass the same concentration range and coincide in lateral extent, showing limited offsite migration. The enhanced aqueous phase partitioning of chromium relative to lead and organics reflects several factors: 1) lead and petroleum hydrocarbons were loaded into the system as a relatively coherent, impermeable mass (oily sludge); 2) formation of low solubility organolead complexes and polymerized organics during the waste-generating processes; 3) formation of low solubility lead carbonate in the calcareous soils; and 4) depletion of more mobile, lower-molecular-weight organic species during the waste-generation processes; this fractionation also increases the viscosity of the residual long-chain aliphatic hydrocarbon mix by eliminating the "fluidizing" components. In contrast, the fact that the shallow groundwater chromium plume coincides with the less mobile lead and petroleum hydrocarbon plumes reflects the very flat hydraulic gradients (0.00013) and low groundwater flow velocities (0.0008 feet/day) that characterize this transmissive system. Hence, dispersion and diffusion rather than advection appear to be the primary mechanisms of contaminant transport.

INTRODUCTION

The Petroleum Products Corporation (PPC) National Priority List site is located in Pembroke Park, Florida, approximately 0.2 mile west of Interstate 95, 1.5 miles north of the Broward County-Dade County line, and 10 miles south of the City of Ft. Lauderdale (Figure 1). The area surrounding the site is highly developed and contains a high-density residential population as well as a variety of commercial/industrial activities. The site lies within the radius of influence of two major municipal well fields: the Hallandale Well Field, approximately 2 miles east-southeast of the site, and the Hollywood Well Field, approximately 3 miles northwest of the site. The combined pumpage at these well fields is on the order of 22 to 27 million gallons per day (GPD).

PPC operated from approximately 1958 to 1971 under various company names as a processor and broker of used petroleum and other hydrocarbon products. Sludges generated by the recycling process were disposed of in unlined pits that covered a fairly extensive area. Between 1970 and 1971, PPC sold most of its property, covered the pits, and reportedly spread contaminated fill across the southern half of the site. After 1971, PPC operations were restricted to the southeast corner of the site, which reportedly functioned only as a storage/distribution facility until complete deactivation in 1985. During this period, the remainder of the original PPC property was developed as commercial/industrial warehouse complex. Several of the warehouses were constructed over the abandoned large primary and smaller secondary disposal pits (Figure 2).

The soils and groundwater underlying the PPC site are heavily contaminated with a variety of inorganic and organic compounds. Lead and long-chain aliphatic petroleum hydrocarbon homologous compounds are by far the predominant soil contaminants. The preponderance of these more complex hydrocarbon compounds prevented the accurate determination of priority pollutant and hazardous substance list organic loads.

Extensive soil contamination is restricted to the southern half of the original PPC property and immediately adjacent areas. This lateral distribution corresponds to the main area of PPC site activity and reflects the extent to which contaminated fill was spread across the site. In the disposal pit areas, highly contaminated sludges occur locally to depths of almost 28 feet; furthermore, at one location elevated contaminant concentrations were still present in the underlying soils 15 feet below the bottom of the pit.

Lead and chromium are the predominant inorganic groundwater contaminants. However, only lead represents PPC-derived contamination; chromium and several associated metals represent at least two different past or present sources of contamination. The groundwater also contains a variety of priority pollutant organic contaminants at low to moderate concentrations.

Lead, chromium, and organic concentrations exceeded State of Florida groundwater standards in a number of the shallow (20-foot) monitoring well samples. The shallow groundwater contaminant plumes in all three cases, however, coincide with the main area of soil contamination and have not migrated very far offsite. The limited extent of contaminant transport is

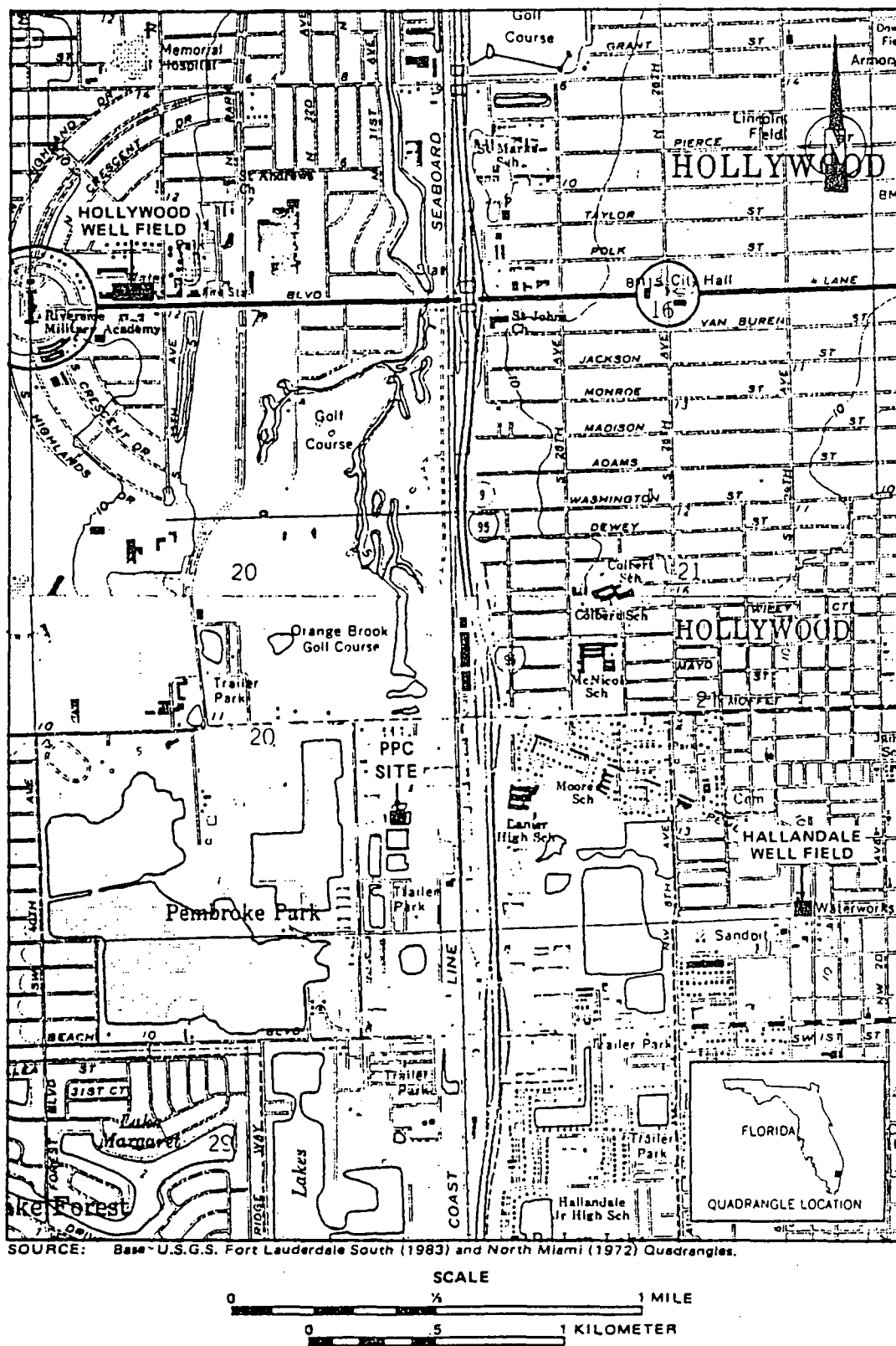


Figure 1 Location of Petroleum Products Corporation (PPC) Site

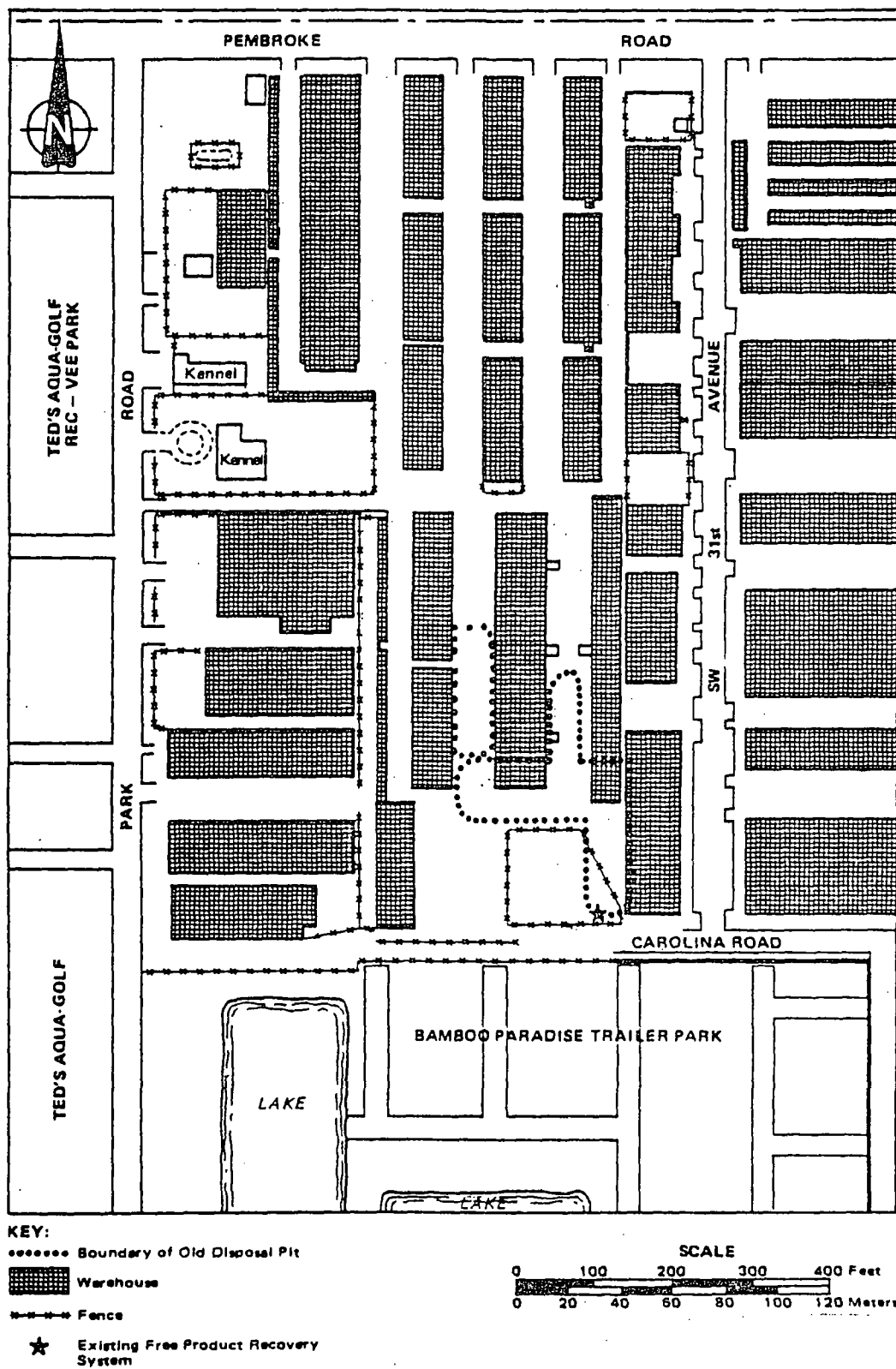


Figure 2 PPC Site Map

primarily controlled by the relatively flat hydraulic gradient (0.00013) and associated low groundwater flow velocity (0.0008 feet/day). In addition, a combination of factors acts to limit the effective mobilization of lead and the organic species from the heavily contaminated soils and sludges. As a result, dispersion and diffusion rather than advection may be the primary mechanisms of contaminant transport.

HYDROGEOLOGY

Regional

The Biscayne Aquifer is the source of all fresh groundwater supplies in Broward County, Florida. The aquifer consists of a highly permeable sequence of interbedded limestones, sandstones, and sands (with interbedded or intermixed clays and marls) that range in age from Late Miocene to Pleistocene. Bearden (1974) and Wedderburn (1982) reported that the aquifer attains a maximum thickness of approximately 200 and 160 feet, respectively, along the coast, thinning to the west. However, more recent work (Cousaras 1985) indicates that the aquifer can be on the order of 500 feet thick in Broward County. The Biscayne Aquifer is underlain by a 500-to 600-foot-thick section of Miocene age marls and clay which separates it from the Floridan Aquifer.

The Biscayne Aquifer exists under water table conditions and is recharged by the direct infiltration of rainfall. Water levels are on the order of 5 feet below land surface. Water table isopleth maps developed by the United States Geological Survey (USGS) for the Biscayne Aquifer in southeast Broward County indicate a regional flow gradient to the northwest and distinct cones of depression associated with the Hollywood and Hallandale well fields which would clearly affect local flow patterns (Figures 3 and 4). The effect of well field pumpage is shown by comparison of the USGS dry season map (May 16-17, 1985; Figure 3) with the wet season map (October 22, 1985; Figure 4). This effect is reflected in increased draw-downs, larger cones of depression, and bowing of the upgradient isopleth between the well fields to create relatively "steep" local hydraulic gradients to the northwest (Hollywood Well Field). Most of the well field production wells are screened at intervals between 50 and 80 feet below land surface, although some screens are set as deep as 152 feet.

Regional hydraulic gradients are extremely flat, rarely exceeding 0.0002 even where well pumpage effects are most pronounced. The Biscayne Aquifer is highly productive, with transmissivities generally exceeding 1 million GPD per foot (Wedderburn 1982). Specific yield is usually estimated at 0.20-0.25, and wells completed in the Biscayne Aquifer can generally be expected to yield up to 7,000 gallons per minute (Wedderburn 1982). Pumpage at the Hallandale Well Field is on the order of 5 to 7 million GPD, and at the Hollywood Well Field on the order of 17 to 20 million GPD.

Site

The upper 8-10 feet of soils in the vicinity of the PPC site consist of a laterally and vertically heterogeneous mixture of calcareous sands,

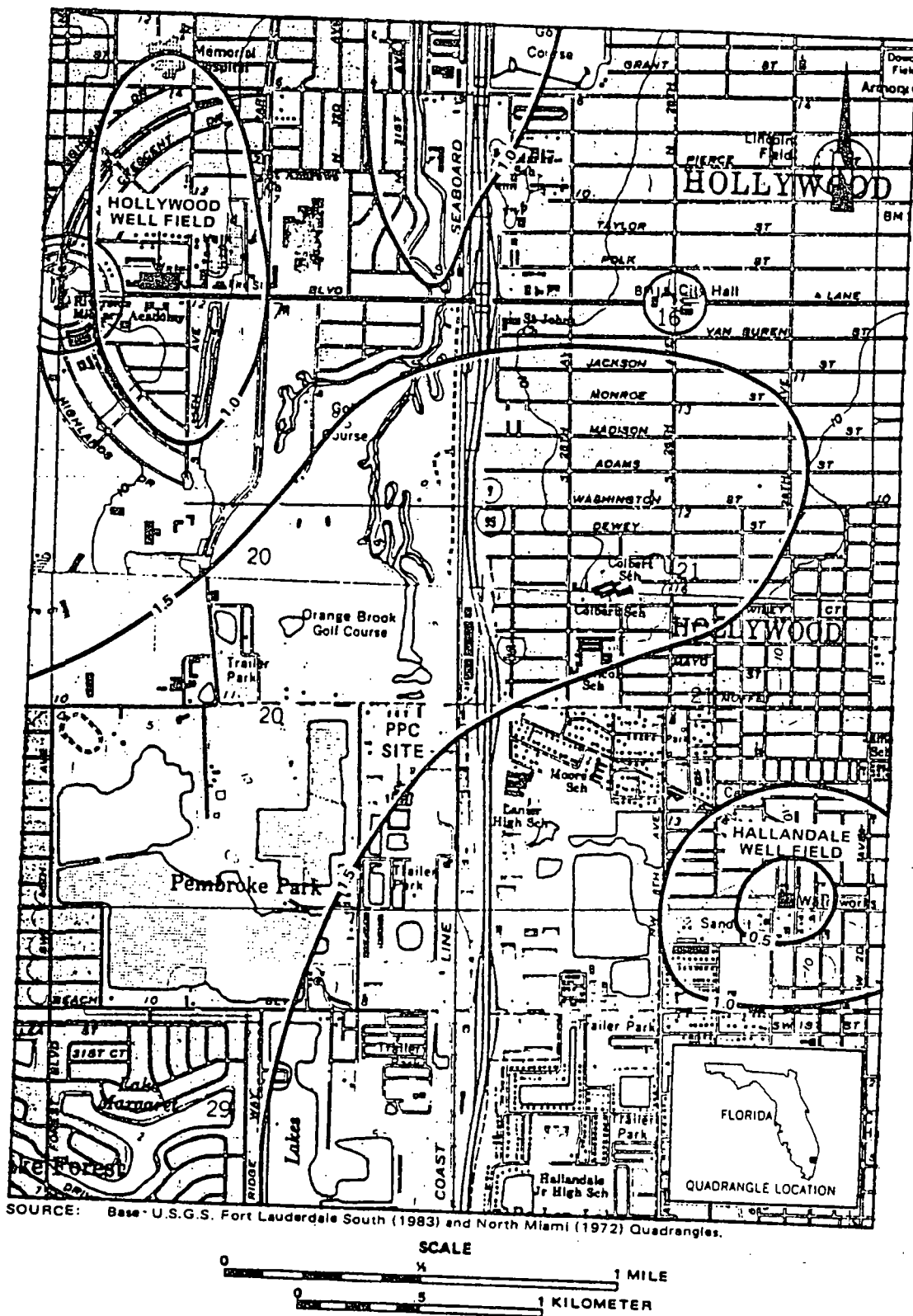
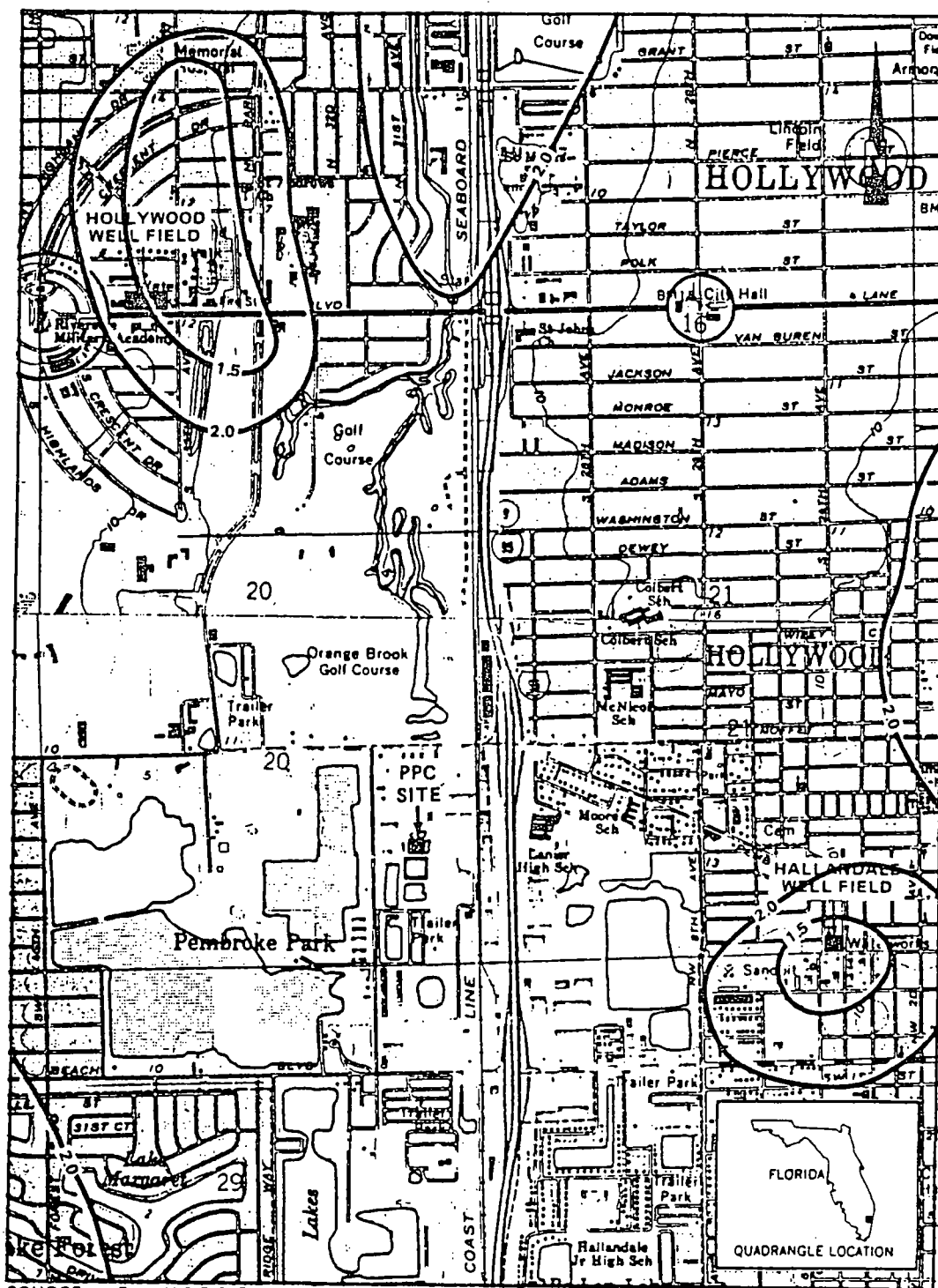


Figure 3 Dry Season Water Level Isopleths (feet above MSL) for the Biscayne Aquifer in Southeast Broward County, May 16-17, 1985



SOURCE: Base- U.S.G.S. Fort Lauderdale South (1983) and North Miami (1972) Quadrangles.

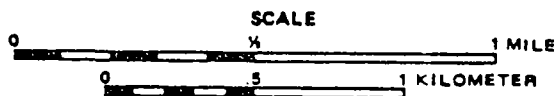


Figure 4 Wet Season Water Level Isopleths (feet above MSL) for the Biscayne Aquifer in Southeast Broward County, October 22, 1985

silts, peat (usually consisting predominantly of vegetative detritus), pebble- and gravel-sized coralline limestone fragments, and occasional layers of clay. The main thickness of the primary disposal pit was defined by a heterogeneous, stratified, complex lithologic sequence of oily calcareous sands and silts, sludge, peat (vegetative detritus), and gravel-sized limestone fragments. Occasionally, non-oily, unstained, "cleaner-appearing" lithologies were interlayered between visibly contaminated horizons. Many of the sludge and peat layers were very dry and even powdery at depths well below the water table. Between 0.5 and 3 feet of seemingly clean fill was present above the visibly contaminated horizons.

The soils underlying the pit were defined by calcareous sands, silts, gravel-sized limestone fragments, and moderately to well-indurated limestones. The heterogeneous stratification of clearly contaminated zones with cleaner-appearing units, combined with the presence of oily or stained horizons at depth, made determination of the actual pit bottom difficult. Hence, the bottom of the pit was determined to be the depth where a more uniform, non-oil-saturated calcareous sequence was encountered, even if materials below this depth exhibited evidence of contamination. The pit is thickest across its central portion (20 feet) and thins out (10-12 feet) along its southern and northern extensions.

The texture of the sludges encountered in the 28-foot-deep secondary disposal pit was unusual in comparison to previously encountered disposal pit lithologies. First, there was very little lithologic stratification; oil-coated calcareous fine sands and silts comprised approximately 85% of the sample by weight. Secondly, these sludges were wet and either plastic or runny, textures that had not been commonly encountered at previous locations, where the sludges were often tight and dry.

The bedrock unit in the area consists of a hard, coral reef limestone that is usually encountered at depths of 10 to 15 feet. This unit is visible in outcrops along the banks of the large excavated lake west of the site. At that location, the unit is present at a depth of 5 feet below land surface. At several shallow monitoring well locations, the limestone bedrock was not encountered by the completion depth (20 feet).

The intermediate and deep monitoring well borings indicated that, above approximately 30 feet, the limestone is intermixed with higher percentages of sand, silt, clay, and shell fragments. This upper unit was described by the driller as a soft limestone, and it was visibly easier to cut through than the underlying harder unit. The coral reef limestone locally has undergone significant post-depositional weathering. This weathering resulted in the formation of a naturally undulatory bedrock surface overlain by a less consolidated, softer, occasionally marly mixture of calcareous sand, silt, and coralline limestone. This overlying unit may have been deposited after the initial weathering of the coral reef limestone or could represent weathering residuum. In either case, land surface topography probably became a subdued reflection of the bedrock surface undulations, with low-lying land areas overlying the bedrock depressions. These areas also may have been subject to subsequent periods of erosion. The PPC primary and secondary disposal pits were probably located to take advantage of these natural low areas and were developed as the operational needs of the facility increased.

The coral reef bedrock limestone sequence is much more permeable than the overlying materials, as evidenced by the drilling mud losses observed upon penetration of the lower unit and confirmed by the results of downhole geophysical logging. Hence, wells screened below a depth of 30 feet should exhibit the pumping characteristics of wells open to the most productive zones of the Biscayne Aquifer. The decreased transmissivity of this upper material reflects the absence of voids and cavities, as well as the fine-grained texture of these soils.

The occurrence and movement of groundwater at the PPC site are influenced by a complex combination of several factors: pumpage at the Hallandale and Hollywood well fields; presence of thick accumulations of relatively impermeable waste sludges that act as barriers to groundwater flow; presence of variable thicknesses of heterogeneous fill material overlying the highly permeable lithologies of the Biscayne Aquifer; asphalt or concrete coverage of large portions of the site, precluding the direct infiltration of rainfall; the presence of local recharge zones as a result of culvert drains and wells, drain fields, and other unpaved areas; and the presence of lakes around the site. These factors interact to produce extremely variable and rapid changes in shallow flow conditions. Figure 5 shows the general water table configuration in the PPC vicinity. However, based on information gathered from the field, it is not these factors that control the migration of contaminants at the PPC site, but rather the nature of the contaminants, the textural characteristics of the contaminated soils, and the very flat lateral and vertical hydraulic gradients.

SITE CONTAMINATION

Soils

Soil data for the PPC site are based on analyses of 0-8 foot soil composites (indicated by circles on Figures 6 and 7) and of 0-5 and 5-10 foot soil composites (indicated by squares on Figures 6 and 7). The latter composite sample sets were obtained to characterize soil contamination above and below the water table. However, the actual sampling intervals were determined not only by the elevation of the water table, but also by the lithologic characteristics of the soils and the presence of contaminated horizons.

The vertical extent of soil contamination was evaluated by means of a series of six deep soil borings within the known disposal pit areas and three deep borings in other areas of known shallow soil contamination. Of these nine borings, eight were conducted to a depth of 20 feet and one, located in the center of the primary disposal pit area, was conducted to a depth of 35 feet. Five of the disposal pit borings were composited to yield samples of soils within and below the pit. The 35-foot disposal pit boring and the three borings outside the pit area were composited to yield samples over five foot intervals.

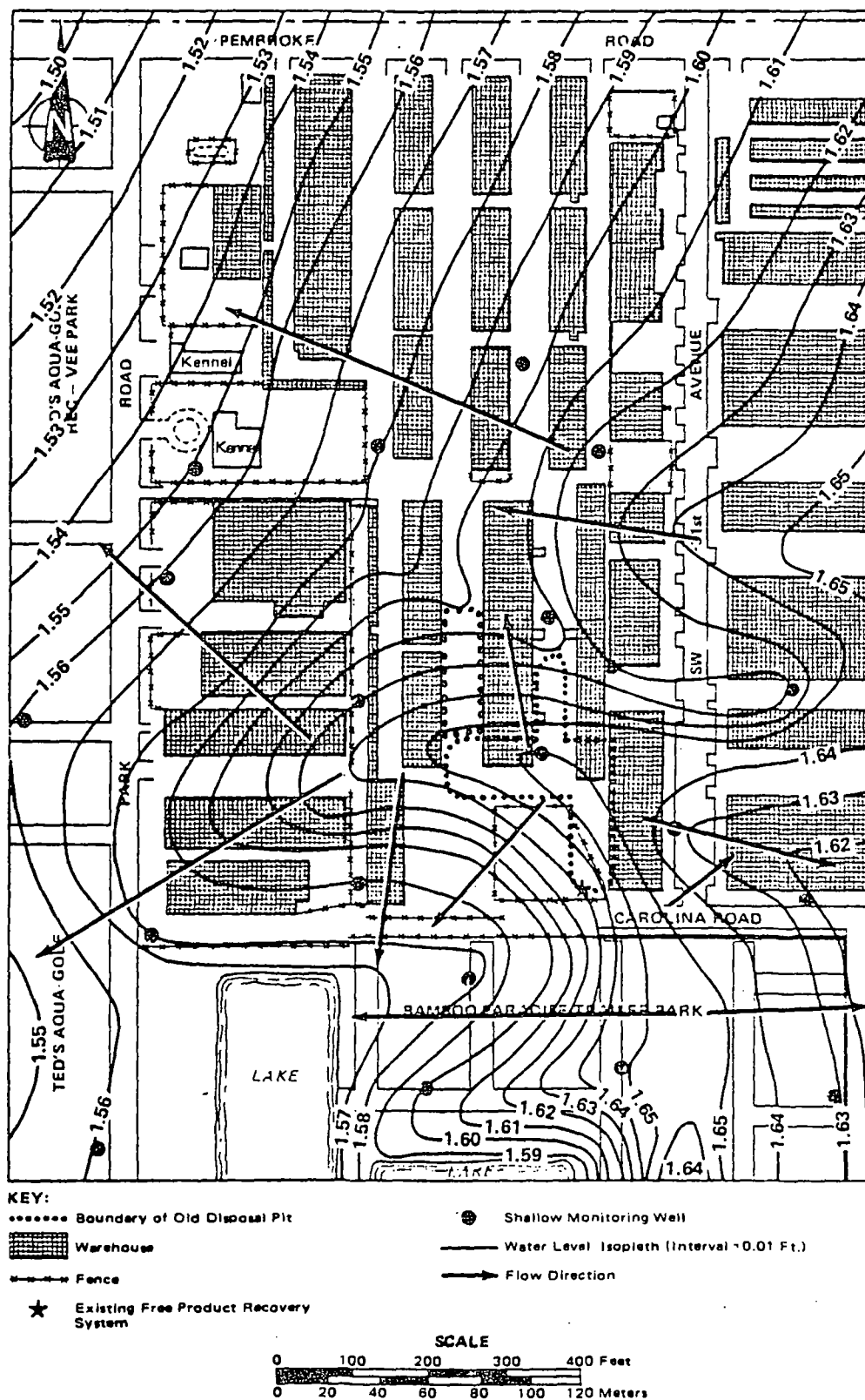


Figure 5. Water Level Isopleth Map Based on Shallow Monitoring Wells, February 27, 1987

Metals

In general, metals that were analyzed for in PPC soils can be divided into three groups:

- Group 1 - Metals that are almost certainly derived from the soil matrix, i.e., calcium, magnesium, sodium, and boron;
- Group 2 - Metals that are almost certainly derived from contaminant sources (although not necessarily PPC-related sources), i.e., antimony, arsenic, barium, cadmium, chromium, cobalt, lead, mercury, nickel, selenium, silver, thallium, vanadium, and cyanide; and
- Group 3 - Metals that could be derived from either the soil matrix or contaminant sources, i.e., aluminum, beryllium, copper, iron, manganese, and zinc.

The Group 1 metals, since they are derived from the soil matrix, were of limited concern.

Several Group 2 metals (cobalt, silver, and thallium) were not detected in any sample, and several others (arsenic, mercury, selenium, vanadium, and cyanide) were detected in a very few samples at concentrations slightly above the detection limits. These metals were thus of limited concern.

Lead was definitely a PPC-related contaminant. The occurrence of the remaining Group 2 metals, i.e., barium, cadmium, and chromium, and Group 3 metals will be evaluated in comparison with lead levels.

Barium, cadmium, and chromium were detected in a number of samples. Cadmium was usually detected only in samples exhibiting high lead concentrations, and never occurred at a level above 10.6 ppm. Consequently, this metal is of limited significance. Barium was also associated with samples exhibiting elevated lead concentrations, but in contrast to cadmium, can attain concentrations as high as 1,500 ppm. However, even in these samples, lead concentrations are at least 4 to 10 times as high as the barium concentrations. Hence, the distribution of barium is reflected in the distribution of the lead. Chromium was present in most samples at relatively low concentrations (<57 ppm), and samples that exhibited relatively elevated chromium concentrations were usually also highly contaminated with lead.

Of the Group 3 metals, beryllium was not detected in any sample. Manganese was present in most samples at low concentrations (<90 ppm), but its occurrence was not associated with that of lead. Consequently, the detected manganese appears to be derived from the soil matrix. Copper was also present at low concentrations (<65 ppm), but was usually detected only in highly lead-contaminated samples. Zinc was found at concentrations as high as 943 ppm in lead-contaminated samples. However, as in the case of barium, the lead levels greatly exceeded the zinc concentrations. Based on the above, it appears that the detected copper and zinc are primarily derived from contaminant sources.

The remaining Group 3 metals, i.e., aluminum and iron, present a more complicated picture. Both metals occur at very high concentrations in soil samples where low concentrations of lead occur. However, the highly lead-contaminated samples exhibit even higher concentrations of iron and aluminum than the soils not contaminated with lead. For example, the mean aluminum and iron concentrations in samples with less than 10 ppm lead are 713 and 1,021 ppm, respectively. In contrast, the mean concentrations in samples with greater than 1,000 ppm lead are 1,688 and 2,407 ppm, respectively. Consequently, aluminum and iron appear to be derived from both the soil matrix and contaminant sources.

In summary, of the entire set of metal parameters, only lead, aluminum, barium, chromium, copper, iron, and zinc appear to be significant soil contaminants. Furthermore, the occurrence of the highest concentrations of aluminum, barium, chromium, copper, iron, and zinc is closely associated with the occurrence of lead, which always appears as the primary metal contaminant. Consequently, lead was the major metal of concern in the soils underlying the PPC site.

Figure 6 delineates the extent of lead contamination of shallow soils across the PPC site; three levels of contamination are delineated: >1,000 ppm; >500 ppm; and >100 ppm.

It is clear from Figure 6 that the area of greatest lead contamination of shallow soils is almost exclusively restricted to the southern half of the site (i.e., the primary area of PPC activity). Outside of this area, only two samples exhibited extremely high lead concentrations (16,900 and 225 ppm). The lithologic logs for these borings provided no indication of a source for these high concentrations. Although it is certainly possible that the detected lead is PPC-derived, the possibility of other local sources cannot be discounted, given the extent of industrial and other activities in the area (e.g., people often change their automobile oil on-site). Several of the other samples outside the main area of contamination exhibit lead concentrations above background, which is estimated at a slightly elevated level of 10 ppm for this area.

Within the main area of contamination, lead concentrations are extremely variable. For example, the five samples collected adjacent to the primary disposal pit exhibit lead concentrations ranging from 347 ppm to 22,400 ppm. Although these results certainly suggest extreme lateral heterogeneity of lead distribution, such results could also reflect: 1) vertical heterogeneity and "dilution" of heavily contaminated zones by less-contaminated horizons during sample compositing, and 2) the difficulty of attaining complete sample homogenization and thus the selection of an unrepresentative aliquot for analysis.

The deep soil borings indicated that elevated lead concentrations were present at depth within and adjacent to the disposal pit areas. At 15-20 feet, lead concentrations as high as 10,700 ppm were detected. The 30-35 foot sample exhibited a lead concentration of 91 ppm, significantly above the background level of 10 ppm.

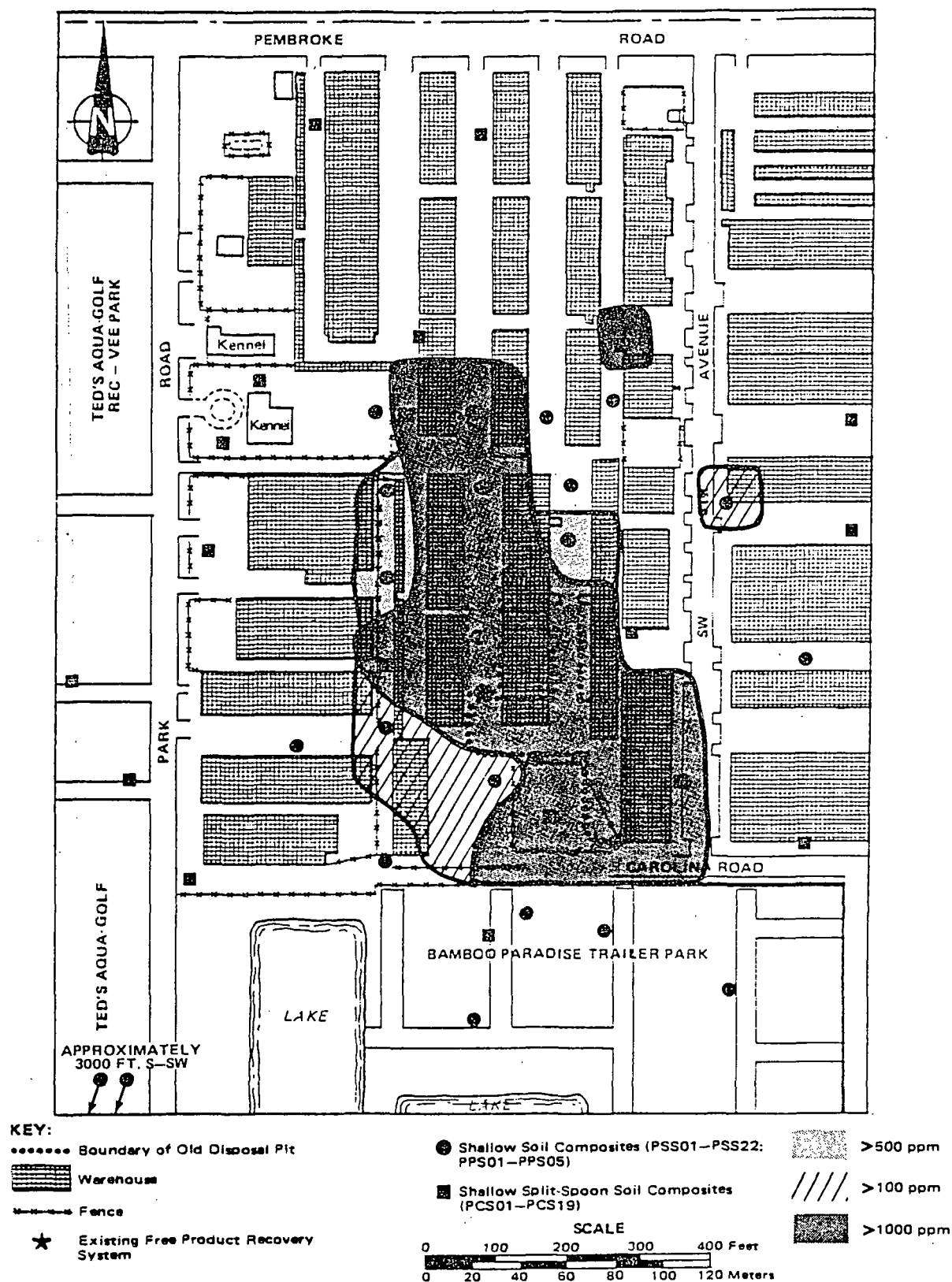


Figure 6 Lead Concentration Areas Based on Shallow Soil Composite Samples and Shallow Split-Spoon Soil Composites

Figure 7 shows the distribution of total organic concentrations in the shallow soils underlying the PPC site and surrounding area. Three levels of contamination are shown: >10,000 ppm; >1,000 ppm; and >100 ppm.

It is apparent from a comparison of Figures 6 and 7 that the distribution of the total organic concentrations closely matches that of lead. Furthermore, as in the case of lead, the organic concentrations vary over a wide range (between 1,000 and 10,000 ppm in the main area of contamination), indicating the potential heterogeneity of contaminant load distribution within the area. However, heavy contamination of the PPC site is generally restricted to the main area in which the facility operated.

Organics

A variety of organic compounds was detected or tentatively identified in a number of the soil samples. However, the distribution and concentration of any one compound are extremely variable, and hence, it is impossible to describe the extent of soil contamination from the perspective of individual compounds. Furthermore, such a description would be very misleading, given that, in general, a major percentage of the contaminant load consisted of hydrocarbon compounds that could not be identified. This was especially true for heavily contaminated samples. For example, examination of the results for the highly contaminated disposal pit samples revealed that the compounds listed under "total unknown hydrocarbons" comprised, on average, 28.5% of the total volatile load and 62.8% of the total semi-volatile and PCB load. Furthermore, the total semi-volatile and PCB load in these samples was generally 17 times greater than the total volatile load. These are the same types of relationships that were exhibited by oil samples collected at the site, and in those samples the total volatile and semi-volatile load accounted for less than 1% of bulk composition.

Based on this general trend, it was determined that organic contamination of soils would be evaluated according to total organic contaminant load. This is not meant to imply that the priority pollutant organics are not of concern at the PPC site, but only that it is almost impossible to present a concise and meaningful description of organic contamination of PPC soils from the perspective of priority pollutant compounds. A number of priority pollutant volatiles, semi-volatiles, and PCBs were detected across the full suite of soil samples. Furthermore, the high total organic loads and associated matrix effects combine to elevate the detection limits for these compounds or otherwise mask their presence.

Similar to lead, the deep soil borings indicated that elevated total organic concentrations were present at depth within and adjacent to the disposal pit areas. At 15-20 feet, total organic concentrations as high as 140,000 ppm were detected. The 30-35 foot sample exhibited a total organic concentration of 1,400 ppm.

Groundwater

Groundwater samples were collected from 22 PVC shallow (20-foot) monitoring wells, 5 PVC intermediate (50-foot) monitoring wells, 2 PVC deep

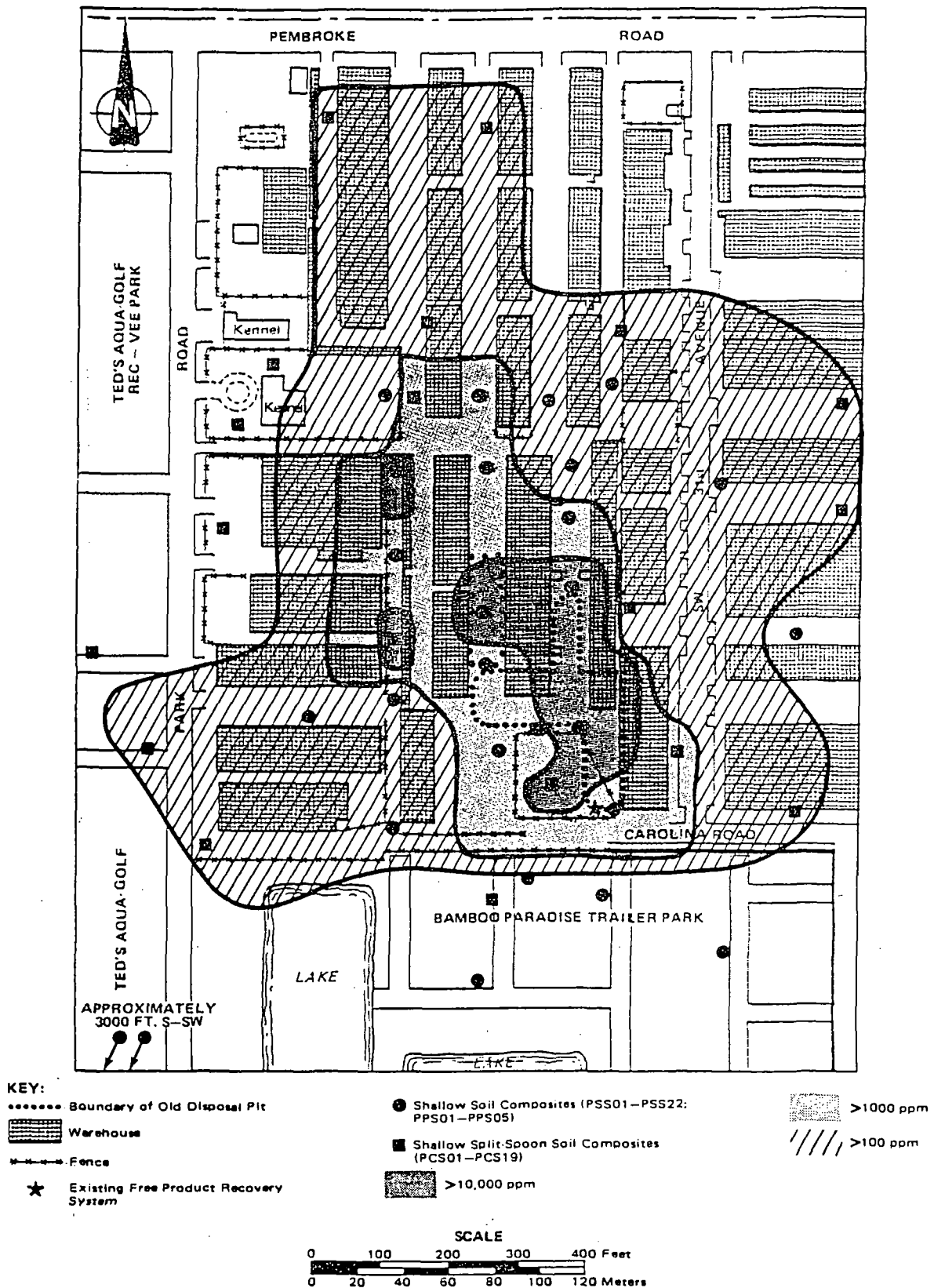


Figure 7 Total Organic Concentration Areas Based on Shallow Soil Composite Samples and Shallow Split-Spoon Soil Composites

(100-and 200-foot) monitoring wells, 5 private wells in the immediate vicinity of the PPC site, and 5 of the culvert drainage wells on the northern half of the site. Of the private wells sampled, one is known to be screened between 101 and 107 feet below land surface, and two are reportedly 57-60 and 75 feet deep, respectively. The depths of the remaining two private wells are not known, but it is believed that they are between 50 and 100 feet deep.

All of the intermediate wells were clustered with shallow wells, and the two deep wells were part of four-well cluster. The culvert drainage wells consisted of 2-inch-diameter PVC pipes with slotted caps and upper casing. These wells had been installed at 10 locations across the northern half of the site below grade in culvert drains, and varied in depth between 40 and 72 feet. The purpose of these wells was to improve surface drainage of the site. Culvert drains were also present on the southern half of the site, but did not contain wells. The discharge point for all of the culvert drains is unknown, and they may simply drain into the subsurface soils. Three runoff water samples were obtained from the southern culvert drains.

Metals

Table 1 summarizes the ranges of individual metal concentrations detected in all classes of water samples collected during this investigation. It is clear from this table that highly elevated metal concentrations were detected primarily in the shallow monitoring wells, drainage wells, and surface water runoff. Boron, calcium, magnesium, sodium, and zinc concentrations were comparatively uniform over all of the sample classes, which suggests that these metals are derived from the soil matrix. However, even for these metals, groundwater samples from the shallow wells appear to exhibit somewhat elevated concentrations, indicating that to some extent these metals may also be derived from a contaminant source. Antimony, cobalt, mercury, thallium, and cyanide were not detected in any sample.

Lead and chromium are the major metal contaminants in the shallow well samples, attaining concentrations of 5,150 ppb and 1,100 ppb, respectively, which greatly exceed the Florida groundwater standard of 50 ppb. Iron and manganese are the only other metals to have been detected at concentrations in excess of established Florida standards (recommended limits of 300 ppb and 50 ppb, respectively). Selenium was present in two samples below the measurable detection limit of 25 ppb, and hence may exceed the Florida standard of 10 ppb. Standards have not been established for several of the metals (aluminum, nickel, and vanadium) present at high levels in the shallow groundwater samples.

There is no direct correlation between the occurrence of high lead and high chromium concentrations (e.g., the sample that contained the highest lead level exhibited the third lowest chromium concentration). This suggests that lead and chromium are not derived from the same primary source. Chromium concentrations were also relatively low in soils with high lead levels.

Table 1

METAL CONCENTRATION RANGES (ppb) IN ALL CLASSES OF COLLECTED WATER SAMPLES

Metal	Shallow Monitoring Wells	Intermediate Monitoring Wells	Deep Monitoring Wells	Private Wells	Drainage Wells	Lakes	Runoff
Aluminum	647 - 376,000	<200 - 2,560	<200	<200	--	<200	--
Antimony	<60	<60	<60	<60	--	<60	--
Arsenic	<10 - 19.8	<10	<10	<10	--	<5	--
Barium	<200 - 447	<200	<200	<200	--	<200	--
Beryllium	<5 - 11.3	<5	<5	<5	--	<5	--
Boron	80.4 - 535	56.1 - 206	65.4 - 120	57.8 - 262	--	63.5 - 104	--
Cadmium	<5	<5 - 6.14	<5	<5	--	<5	--
Calcium	88,200 - 2,020,000	82,800 - 129,000	66,300 - 64,800	71,300 - 95,200	--	17,300 - 89,300	--
Chromium	<10 - 1,100	<10 - 11.3	<10	<10	33 - 1,760	<10 - 13.2	<10
Cobalt	<50	<50	<50	<50	--	<50	--
Copper	<25 - 107	<25	<25	<25	--	<25 - 70.8	--
Iron	1,960 - 77,100	207 - 757	175 - 283	1,080 - 7,930	--	<100 - 162	--
Lead	<5 - 5,150	9.2 - 22.1	<5 - 13.3	<5 - 10.9	627 - 5,990	<5 - 8	<10 - 320
Magnesium	3,540 - 92,200	2,790 - 17,300	3,250 - 5,810	1,720 - 6,690	--	1,540 - 4,180	--
Manganese	57.1 - 308	<15	<15	<15 - 30.9	55 - 362	<15	<15 - 60
Mercury	<0.2	<0.2	<0.2	<0.2	--	<0.2	--
Nickel	<40 - 174	<40	<40	<40	--	<40	--
Selenium	<5 - <50 (<25)	<5	<5	<5	--	<5	--
Silver	<10 - 12.2	<10	<10	<10	--	<10	--
Sodium	5,780 - 44,300	14,700 - 37,300	18,200 - 55,800	9,320 - 17,500	--	7,900 - 11,600	--
Thallium	<5	<5	<5	<5	--	<5	--
Vanadium	<50 - 239	<50	<50	<50	--	<50	--
Zinc	45.4 - 379	<20 - 112	<20 - 53.6	<20 - 492	--	<20 - 33.4	--
Total Cyanide	<10	<10	<10	<10	--	<10	--

Table 2

CORRELATION BETWEEN CHROMIUM AND OTHER METALS
IN GROUNDWATER SAMPLES

Sample	Cr	Al	Be	Fe	Ni	V
PMW08A	1,100	376,000	10.2	77,100	174	239
PMW10AD	580	192,000	7.3	61,400	62.6	194
PMW10A	519	171,000	6.1	59,600	69.6	167
PMW03A	474	202,000	6.1	27,000	80.4	83
PMW04A	468	169,000	11.3	34,600	110	156
PMW01A	218	93,400	<5	19,000	47.2	59.3
PMW07A	193	60,500	<5	15,900	43.2	<50
PMW02A	139	44,100	<5	11,700	<40	56.2
PMW05A	35.9	10,500	<5	5,250	<40	<50
PMW12A	23.4	5,680	<5	3,210	<40	<50
PMW11A	13.7	3,600	<5	1,950	<40	<50
PMW06A	<10	647	<5	8,130	<40	<50

In general, only the zinc and barium concentrations appear to correlate with lead; however, this correlation is not very well-defined. In contrast, five metals (aluminum, beryllium, iron, nickel, and vanadium) exhibit an extremely well-defined correlation with chromium. The co-occurrence of these metals is readily seen from the list of sample metal concentrations presented in order of decreasing chromium concentrations in Table 2.

The Table 2 correlations become extremely significant given that the three highest lead concentrations (5,150; 2,580; and 1,800 ppb) are all associated with relatively low chromium concentrations. Given that the oil sludges and contaminated soils clearly associated with the PPC operation exhibited relatively low concentrations of chromium compared to lead, it is clear that the chromium and associated metals in the shallow groundwater samples are not derived from the same source as the lead. Hence, the presence of lead in soils and groundwater is direct evidence of PPC-derived contamination within the immediate area of the site.

Moreover, not only does it appear that there must be more than one source of chromium and associated metals within the immediate site area, but there must also be a source of these metals and lead at the background sample location. The requirement of two sources on the warehouse reflects the wide separation between the main areas of chromium contamination: immediately north-northeast of the disposal pit areas (519-1,100 ppb), and in the southwest corner of the warehouse complex, extending onto the Bamboo Paradise Trailer Park (468-474 ppb). The north-northeast location is within an area of varied activities, but no specific contaminant source has been identified. In contrast, the southwest location is in the immediate vicinity of both a former anodizing plant and a former spray-painting operation currently under a separate enforcement action. Either of these former facilities would constitute likely sources.

It is clear that a source of contamination must also be present at the background location, approximately 3,000 feet south-southwest of the site. This sample contained high levels of both lead and chromium (161 ppb and 218 ppb, respectively) as well as elevated concentrations of the metals that accompany chromium. Although the presence of contamination in a background location within an active commercial/industrial area is not unusual, it is surprising how well the metal concentrations detected fall into the chromium-related trend discussed above. It would seem that the all three contaminant sources must be very similar in nature.

It is important to note that the elevated concentrations of such metals as aluminum and iron reflect active contamination sources rather than merely input from the soil matrix. This is evidenced by the fact that the detected concentrations in chromium-contaminated samples are so much greater than those in samples containing little chromium. Additional evidence for the absence of large soil matrix input is provided by the data in Table 1, which shows that these extremely high concentrations are only observed in shallow monitoring well samples. Aluminum and iron (but not beryllium, nickel, or vanadium) were present at high concentrations in both lead-contaminated and non-lead-contaminated samples; however, the concentrations are usually higher in the lead-contaminated samples.

Figures 8 and 9 show the areas of lead and chromium contamination of shallow groundwater in the vicinity of the PPC site, respectively. Two levels of contamination are shown: concentrations greater than the Florida groundwater standard (50 ppb in each case) and concentrations greater than the detection limit (5 ppb for lead, and 10 ppb for chromium), which is assumed as the background level. Comparison of Figures 8 and 9 shows that the shallow lead and chromium contaminant plumes are almost identical in extent. More importantly, neither plume has migrated very far from its respective source area or areas.

Comparison of these figures with the extent of lead contamination of shallow soils shown on Figure 6 indicates that the areas of shallow groundwater and soil contamination closely coincide. However, whereas lead apparently preferentially remains fixed in the soil phase, chromium and the associated metals are more readily mobilized. Hence, lead and chromium exhibit similar concentration ranges in the groundwater despite extreme differences in their soil concentrations. The comparative immobility of

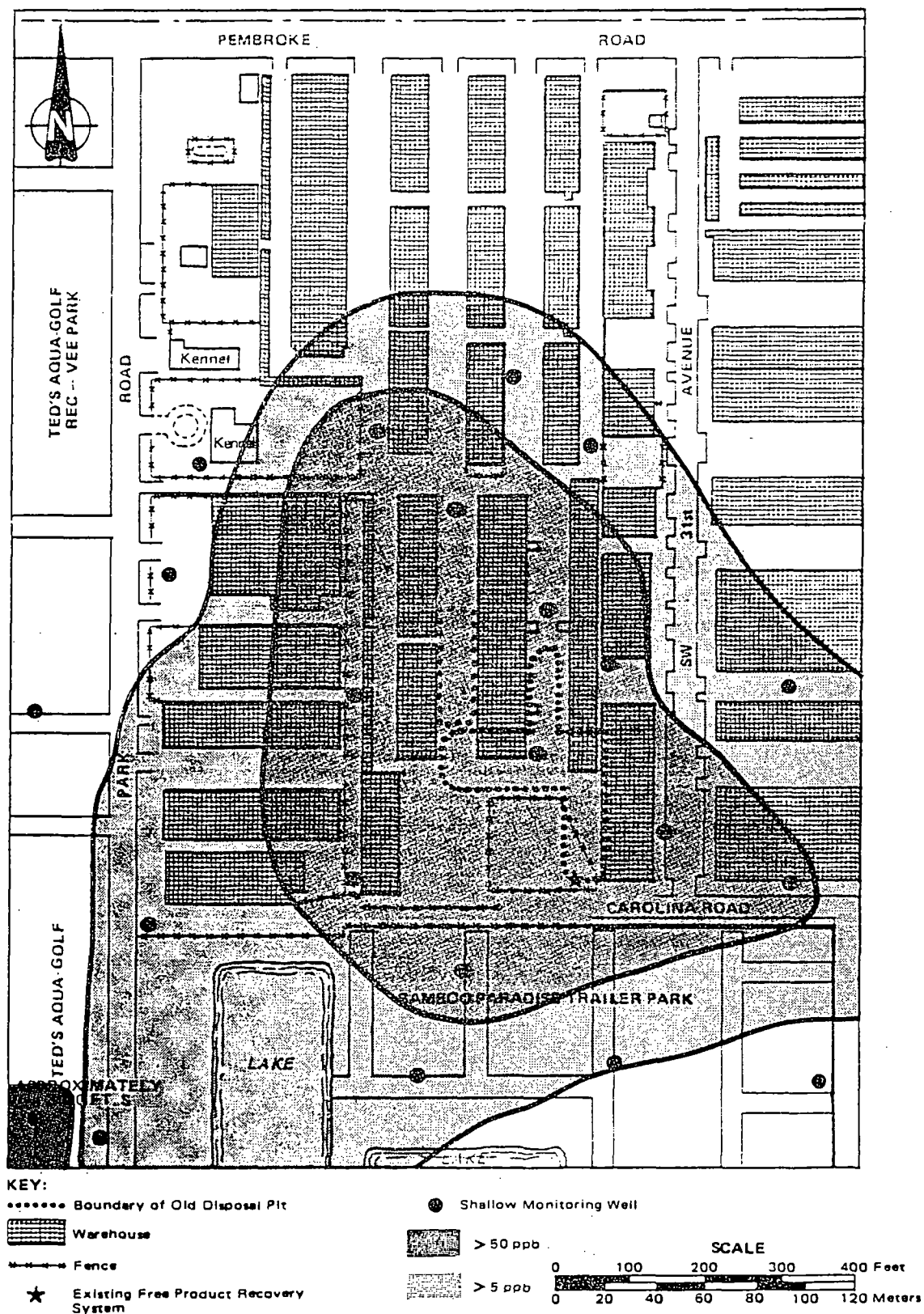


Figure 8 Lead Concentration Areas Based on Shallow Monitoring Wells

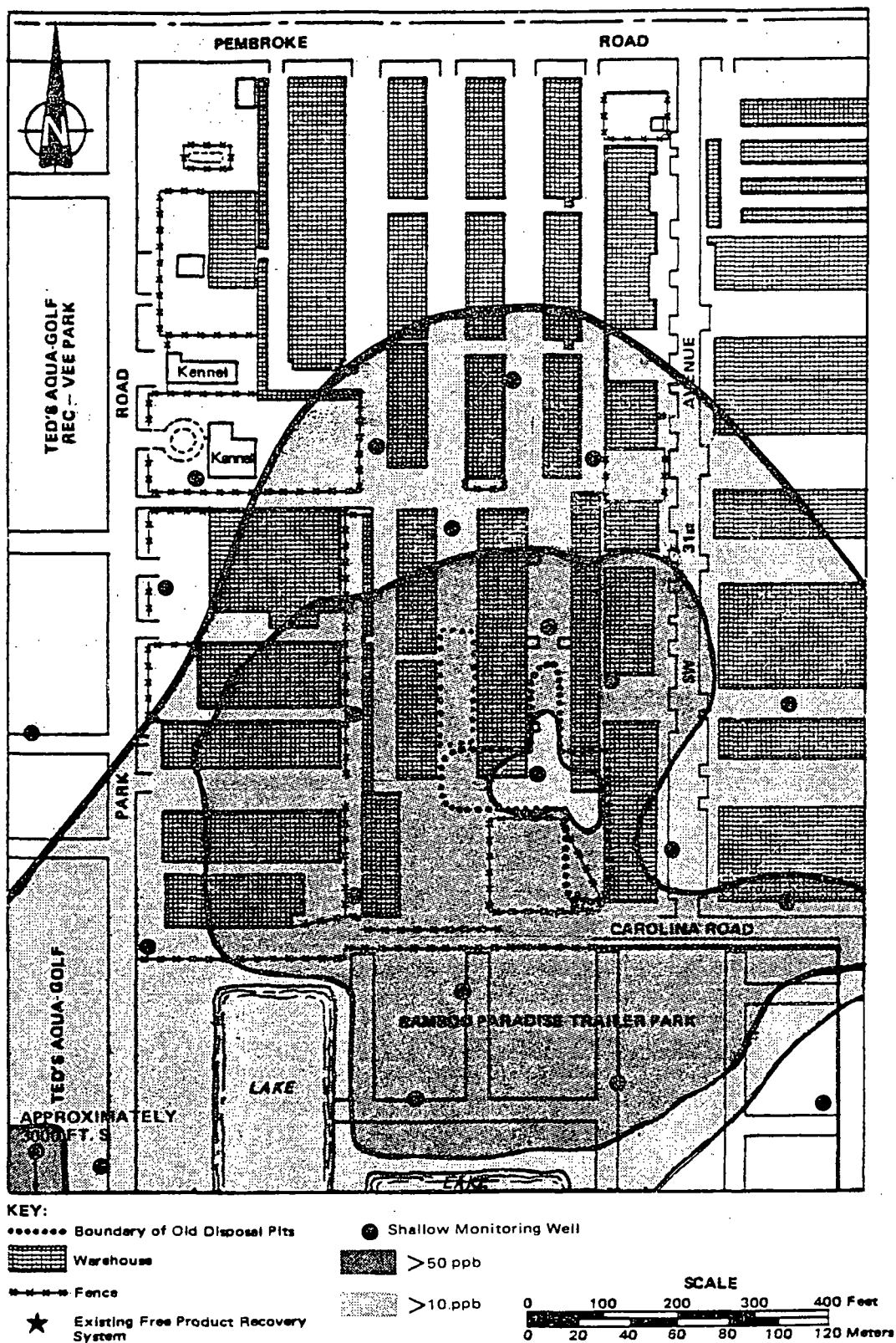


Figure 9 Chromium Concentration Areas Based on Shallow Monitoring Wells

lead is believed to result from: 1) complexation with the organic contaminants; 2) formation of relatively insoluble lead carbonate complexes; and 3) its amphoteric properties. The formation of organolead complexes is inherent to the generation of oil reprocessing wastes (i.e., they were probably already formed even before disposal), whereas organic complexes of the other metals would not have been formed until the various species came into contact in the subsurface. Hence, it might be suspected that organolead complexes would predominate at the PPC site. The highest lead concentrations in shallow groundwater were in sampling locations proximate to the primary and secondary disposal pit areas.

To some extent, the more or less concentric distribution of the lead and chromium contaminant plume boundaries reflects the radial distribution of shallow flow components around the disposal pit area (see Figure 5). However, given the extremely flat hydraulic gradients and low groundwater flow velocities that characterize the shallow flow system, it is also probable that the concentric distribution--as well as the very limited degree of lateral migration--reflects the fact that dispersion and diffusion rather than advection are the primary mechanisms of contaminant transport. This will be discussed in greater detail below.

The culvert drain runoff samples were contaminated with lead and chromium. Although this pathway may be very significant with respect to chromium contamination of shallow groundwater, it is believed to be secondary to the contaminated soils as a source for lead.

The analytical results for the intermediate monitoring well and private well samples indicate only limited vertical migration of contaminants into the more transmissive zones of the Biscayne Aquifer. Lead and chromium concentrations were generally below detection limits. However, a lead concentration of 22 ppb was detected in an intermediate well installed in an area of high shallow groundwater contamination. In contrast, the 80 ppb chromium concentration detected in the northernmost intermediate well is not associated with high chromium levels in the shallow groundwater. It is believed that this contaminant was introduced directly into the intermediate groundwater system via the culvert drainage wells located on the northern half of the site, all of which contained very high concentrations of chromium and lead. However, the culvert drainage wells are located down-gradient of the chromium-contaminated intermediate well. Hence, dispersion and diffusion rather than advection are in this case also the most probable mechanisms of contaminant transport. The absence of comparatively elevated lead concentrations in the chromium-contaminated intermediate well probably reflects the reprecipitation of lead carbonate.

Organics

Organic contamination of groundwater at the PPC site is essentially restricted to the shallow zone (however, as in the case of the metals, the culvert drainage well samples are highly contaminated with petroleum hydrocarbons). The shallow groundwater samples exhibited sporadic occurrences of low to moderate concentrations of a variety of priority pollutant volatile species as well as the more complex long-chain aliphatic hydrocarbons. The sample from PMW06A, screened below the bottom of the primary disposal

pit, contained the highest total volatile concentration (1,198 ppb), including 300 ppb acetone, 250 ppb 2-butanone, and 370 ppb ethanol (possibly derived from the isopropanol used to initially decontaminate the bailers). Dilution of this sample was required, which elevated the detection limits by a factor of 5 and possibly accounted for the elevated levels of acetone and methylene chloride. The remaining samples all contained less than 264 ppb total volatile organics.

The highest concentration of semi-volatile compounds detected was 2,303 ppb, but this includes 480 ppb bis (2-ethylhexyl) phthalate, a common laboratory-derived contaminant, and 1,300 ppb molecular sulfur. Only two other samples contained greater than 1,000 ppb semi-volatiles (1,137 ppb, including 780 ppb molecular sulfur, and 1,653 ppb, including 140 ppb molecular sulfur and 194 ppb total phenols).

Figure 10 shows the primary area of total organic contamination (>1,000 ppb) across the PPC site. The extent of organic contamination of shallow groundwater generally coincides with the lead and chromium groundwater plumes (see Figures 8 and 9) as well as with the extent of organic contamination in the shallow soils (see Figure 7). Hence, the processes that control the extent of the metal contaminant plumes in the shallow groundwater also control the extent of organic contamination. However, comparison of the shallow groundwater and shallow soil organic concentrations indicates that organics are even less mobile than lead (based on comparison of their respective concentrations in soils and groundwater). The relative immobility of the organics is not surprising, given that long-chain aliphatic petroleum hydrocarbons are by far the predominant organic contaminants on the PPC site. These compounds are inherently less mobile than, for example, the priority pollutant organics by virtue of their higher molecular weights. Moreover, the mobility of the long-chain hydrocarbons is decreased even further by the depletion of the lower-molecular-weight, more volatile compounds required to maintain a less viscous composition. Finally, the mobility of the long-chain hydrocarbons can also be reduced if any polymerization has occurred, either during processing or after disposal.

The priority pollutant analyses for the groundwater samples were not as subject to interferences as were the soil sample analyses. The primary reasons for this are the generally low total organic concentrations in the groundwater, as well as a much reduced number of detectable compounds that produce interfering peaks. Consequently, in contrast to the corresponding soil sample results, the results of the priority pollutant analyses for the shallow groundwater samples are probably more representative of the actual occurrence of these compounds in the aqueous phase at the PPC site. The occurrence of low priority pollutant concentrations in the groundwater, in contrast to their presumed presence at significantly higher concentrations in the soils, probably reflects the fact that their mobilities are reduced via interaction with the more complex long-chain hydrocarbons. However, eventual degradation of these compounds could lead to release of priority pollutant species, and hence, an increase in groundwater contamination cannot be dismissed as a potential long-term effect.

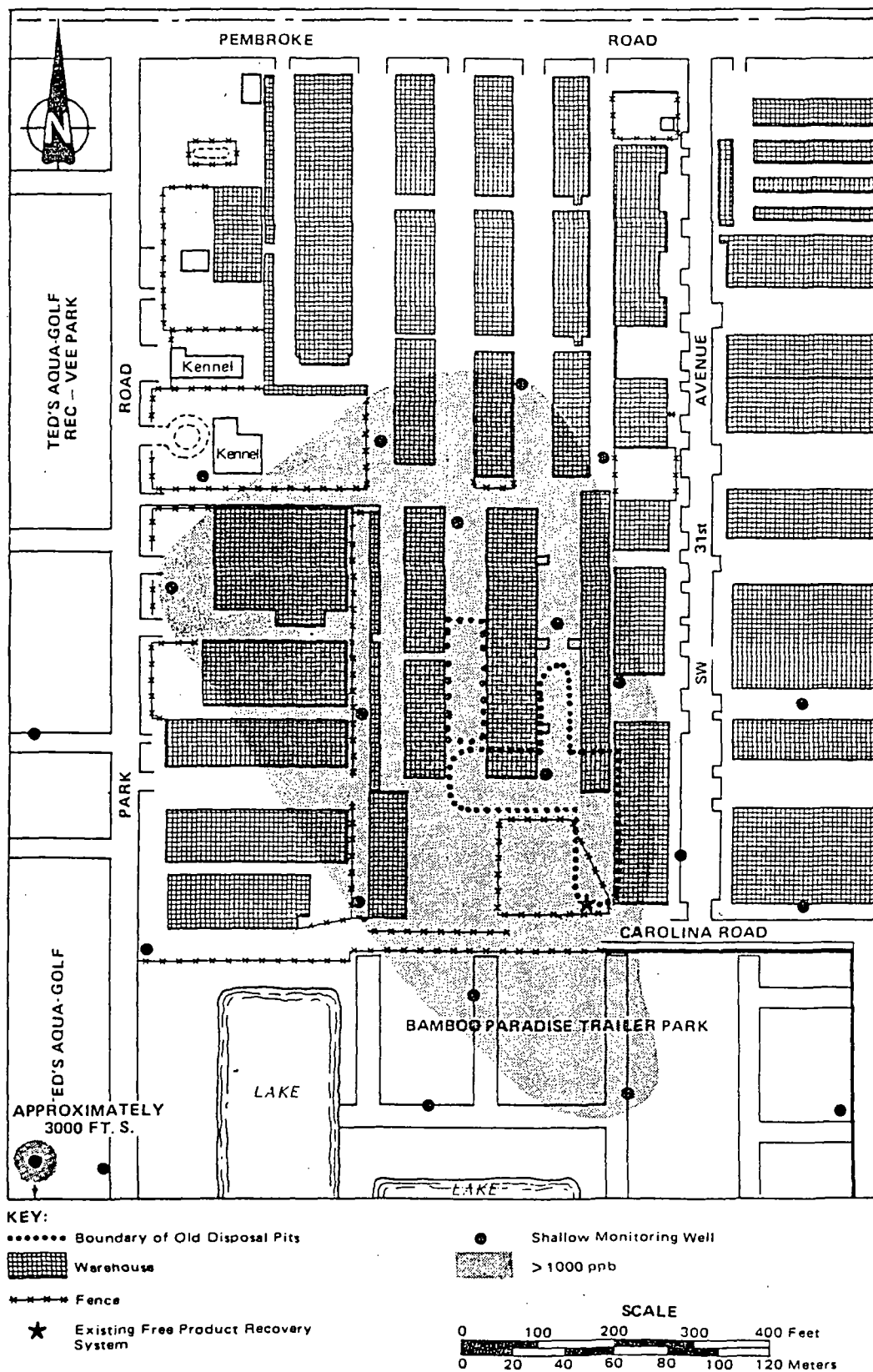


Figure 10 Total Organic Concentration Areas Based on Adjusted Concentrations in Shallow Monitoring Wells

CONTAMINANT TRANSPORT

The factors that control contaminant transport at the PPC site include loading of contaminants into the subsurface, partitioning of contaminant species between the soil and groundwater, and mechanisms of contaminant transport in groundwater. With respect to contaminant loading, two associations of chemical species are found at the PPC site: lead/petroleum hydrocarbons and chromium/associated metals. The importance of this finding is that it implies different sources and also different "source media." Lead and petroleum hydrocarbons are predominantly a signature of PPC-derived wastes, whereas the chromium and associated metals are apparently derived, for the most part, from other sources. Moreover, lead and petroleum hydrocarbons appear to have been primarily loaded as a relatively coherent mass in viscous waste oil, sludge, and oil-saturated soils. In contrast, chromium and the associated metals seem more likely to have been primarily loaded in the form of more widely dispersed liquid wastes. The difference in source media suggests that chromium and the associated metals would inherently be present at proportionately higher concentrations than lead in groundwater, relative to concentrations in soils.

Furthermore, due to the loading of lead and petroleum hydrocarbons in a coherent, low-permeability mass, these contaminants will not be 100% accessible to leaching by groundwater. This in itself would significantly reduce the partitioning of lead and petroleum hydrocarbons into the aqueous phase. However, its effect is enhanced by several other factors, namely:

1. The presence of large paved areas that prevent the direct infiltration of rainfall;
2. The formation of low solubility organolead and polymerized organic complexes, which probably develop to a large extent during the waste-generating processes, and hence, are directly loaded into the system;
3. The predominantly calcareous soil matrix, which favors the development of low solubility lead carbonate complexes;
4. The amphoteric properties of lead;
5. The depletion of the more mobile, lower-molecular-weight organic species during the waste-generating processes; this fractionation not only removes the most soluble organic species (including many of the priority pollutants), but also increases the viscosity of the residual long-chain aliphatic hydrocarbons by eliminating these "fluidizing" components; and
6. The waste-generation processes specified above include not only those associated with the PPC operation, but also those which generated the raw material wastes reprocessed by PPC (in particular, combusted motor oils).

Only the first three of these factors would affect the partitioning of chromium and associated metals, and in all cases the effect of these factors would be less severe with respect to chromium and its associated metals than with respect to lead and petroleum hydrocarbons. For example, the lack of directly infiltrating rainfall is less important because these contaminants have not been loaded as a coherent mass. Similarly, whereas organolead complexes probably have already formed in the reprocessed wastes before loading, formation of the organochromium and other organometallic complexes requires that the organics and metals come into contact; furthermore, the magnitude of this effect is limited by the low permeability of the organic-rich sludges. Finally, the other possible metal carbonate compounds are more soluble than lead carbonate. In summary, it is perhaps simplest to consider that the partitioning of lead and petroleum hydrocarbons occurs in transition from the soils to the groundwater, whereas the partitioning of chromium and the associated metals occurs in transition from the groundwater to the soils.

The above discussion of partitioning considers factors that control the relation between groundwater contaminant concentrations and the corresponding soil contaminant concentrations. However, it does not adequately consider the factors that control the migration of contaminants away from the primary source areas. It is evident that such factors must exist, since despite all the mechanisms that would act to prevent initial partitioning into the aqueous phase and favor re-fixation onto the soil matrix, localized occurrences of very high contaminant concentrations occur in the groundwater. Re-fixation processes (e.g., adsorption and precipitation) do not occur instantaneously, and hence, the degree to which migration of a given contaminant will actually be retarded is dependent not only on the retardation factor, but also on the groundwater hydraulic gradient and groundwater flow velocity. In other words, the limited contaminant plume extents at the PPC site not only require the presence of an inherent retardation factor, but also a flat hydraulic gradient and low groundwater flow velocity—both of which characterize the lateral and vertical components of groundwater flow at the PPC site. If these flow parameters were not controlling contaminant migration, the lead, chromium, and organic plumes would not correspond as closely as they do, since their mobilities (i.e., degrees of retardation) are different. Thus, lateral and vertical contaminant migration at the PPC site are as likely to be determined by dispersion and diffusion as by advection.

The importance of dispersion and diffusion in controlling contaminant transport at the PPC site is suggested not only by the coincidence of all three contaminant plumes and their limited extent of migration, but also by the concentric distribution of these plumes around the primary source areas. In other words, there is absolutely no evidence of linear transport of contaminants from groundwater "hotspots," but rather elevated contaminant concentrations are radially distributed around these locations. This type of distribution is not consistent with advection as the controlling mechanism of contaminant transport.

Although the relationships above unquestionably define the overall distribution of contamination at the PPC site, they cannot be invoked to explain the many anomalies that appear in the data set. These anomalies probably reflect such influences as surface water runoff contamination

sources and other local sources of contamination associated with current onsite activities; septic tank and sewer line leakage; and locally enhanced mobilization of contaminant and soil matrix species by acidic wastes derived from the use of the sulfuric acid process by PPC to reclaim used motor oil. However, these anomalies are minor when viewed from the perspective of the overall distribution of the contaminant load and the systemic processes that shape it.

CONCLUSIONS

Former recycling operations at the PPC site have resulted in extensive contamination of soils and groundwater by lead and petroleum hydrocarbons. In addition, other past and current site activities are loading these contaminants as well as chromium and associated metals directly into the groundwater system. Despite the different mobilities and soil concentrations of these contaminants, they all exhibit similar concentration ranges in the groundwater, similar concentric distributions around the primary source areas, and similar limited degrees of offsite migration. These similarities of contaminant occurrence are associated with: 1) the different loading histories, which—in combination with several other factors—limits the partitioning of lead and organics into the aqueous phase; and 2) the extremely flat hydraulic gradient and low groundwater flow velocity of this groundwater system, which result in dispersion and diffusion rather than advection acting as the primary mechanisms of contaminant transport.

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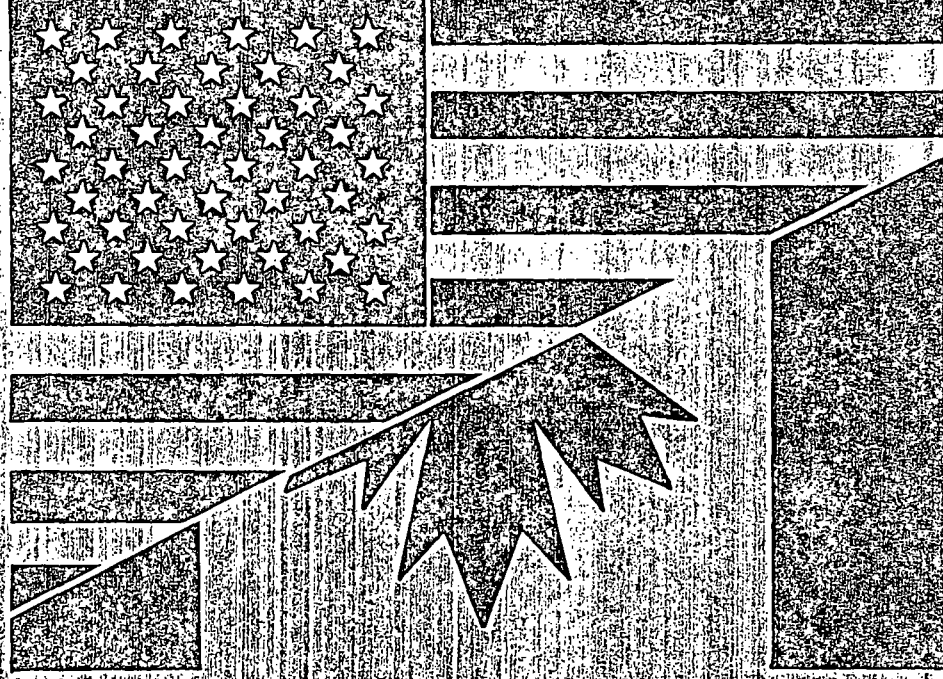
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Interactions of Acidic Solutions With Sediments: a Case Study

by S.R. Peterson, R.J. Serne, A.R. Felmy, R.L. Erikson, K.M. Krupka and G.W. Gee

Abstract

A methodology is presented for investigating the chemical interactions of acidic solutions with sediments. This approach illustrates how geochemical modeling can be used, in parallel with characterization data for sediments from field and laboratory experiments, to derive a composite description of the solution/sediment interactions. The MINTEQ geochemical computer code was used to predict solid-phase reactions that might occur when acidic solutions contact neutral sediments, which, in turn, may control the concentrations of certain dissolved components. Results of X-ray diffraction analysis of laboratory samples of sediments that have been contacted with acidic uranium mill tailings solutions suggest gypsum and jarosite precipitated. These same mineralogical changes were identified in sediment samples collected from a drained uranium mill evaporation pond (Lucky Mc mine in Wyoming) with a 10-year history of acid attack. Geochemical modeling predicted that these same phases and several amorphous solids not identifiable by X-ray diffraction should have precipitated in the contacted sediments.

An equilibrium conceptual model consisting of an assemblage of minerals and amorphous solid phases was then developed to represent a sediment column through which uranium mill tailings solutions were percolated. The MINTEQ code was used to predict effluent solution concentrations resulting from the reactions of the tailings solution with the assemblage of solid phases in the conceptual model. The modeling

predictions were compared to the measured column effluent concentrations, and hypotheses were formed as to the probable mechanisms controlling the migration of selected contaminants. The conceptual model successfully predicted the concentrations of several of the macro-constituents (e.g., Ca, SO_4 , Al, Fe and Mn), but was not successful in modeling the concentrations of trace elements. The lack of success in predicting the observed trace metal concentrations suggests that other mechanisms, such as adsorption, must be included in future models. The geochemical modeling methodology coupled with the laboratory and field studies should be applicable to a variety of waste disposal problems.

Introduction

Disposal of uranium mill tailings is likely the most difficult technical challenge presently faced in solving the nuclear waste problem (Cunningham 1978). The technical challenge lies in adequately handling massive volumes of leachable, low level radioactive wastes, which exceed the amount of any other wastes generated in the nuclear fuel cycle. The quantity of uranium mill tailings in the United States is approximately 1.8×10^8 metric tons and this amount is expected to double by the year 2007 (Oak Ridge National Laboratory 1983).

The seepage of acidic leachate from disposed tailings is potentially hazardous at sites where wastes are disposed in impoundments with high permeability and low-acid neutralizing capacities, or with small distances between the tailings and existing water tables. In Canada, the Elliot Lake and Bancroft areas have

had the water quality adversely affected by the migration of tailings solution (Brown et al. 1981) and in the United States, contamination of surface and/or ground water has also occurred (e.g., Cannon City, Colorado [Cotter]; Ford, Washington [Dawn Mining]; Gas Hills, Wyoming [Union Carbide]). Details of these occurrences are described in a Mineral Resources Waste Management Team report (1980).

To better understand such water quality degradation, we have used experimental and computer modeling techniques to assess the long-term environmental impact of leachate movement from uranium mill tailings impoundments. Specifically, laboratory experiments and geochemical computer codes were used to evaluate the migration potential of selected contaminants (both radioactive and toxic elements) from uranium mill tailings leachate in contact with sediments and geologic liner materials.

The principal issues addressed by our experimental and geochemical modeling study include: (1) the short- and long-term mineralogical and hydrological changes that occur when acidic tailings solutions contact sediments; (2) the identification of contaminants that will migrate from uranium mill tailings impoundments and the sediment/solution interactions responsible for the attenuation of these contaminants; and (3) the prediction of contaminant concentrations in the migrating solution and ground water systems.

The specific issues discussed in this document are:

- Can laboratory and geochemical modeling techniques be used to simulate chemical processes that occur in the field?
- Can a conceptual chemical model be used to predict the concentrations of selected contaminants that result from tailings solutions reacting with a sediment column?

A system consisting of uranium mill tailings solution, of low pH and high dissolved solids, in contact with clay sediments was chosen as a test for our predictive modeling study. In this system, precipitation/dissolution of solid phases is expected to be the dominant mechanism controlling the concentrations of several dissolved constituents. The contaminant concentrations predicted by our conceptual model were compared to experimental data from laboratory flow-through columns; the mineral phases predicted from the solution/mineral interactions were similarly compared to laboratory studies and to field samples from an inactive tailings pond.

Background and Objectives

Crim et al. (1979) measured increases in the permeability of montmorillonite clays subjected to extended contact with an acidic ($\text{pH} < 1$) tailings solution. These changes in permeability varied by more than two orders of magnitude, but tended to increase most dramatically after the pH of the effluent dropped below four (from an initial value near eight). Gee et al. (1980a, b) and Peterson et al. (1982) studied

the effects of extended contact of acidic tailings solution ($\text{pH} = 2$) on the permeability of native clays from Morton Ranch mine in central Wyoming. Their results indicate the permeability of the clays gradually decreased with time during contact periods extending up to three years. Because the clay material exhibited little physical evidence of deterioration, they partly attributed the decreases in permeability to the precipitation of iron and aluminum solid phases and possibly of secondary clay minerals stable at $\text{pH} < 3$. In addition, Relyea and Martin (1982) reported dramatic (up to three orders of magnitude) decreases in permeability after contacting highly calcareous soils with acidic tailings solutions. They also attributed the decrease in permeability to the precipitation of solid phases. Langmuir and Piese (1981) predicted that amorphous ferric hydroxide would begin to precipitate around pH 2 in uranium mill tailings. This precipitation, as a slime, was thought to help reduce seepage away from the tailings impoundments.

Ion-speciation and solid-phase solubility calculations have been extensively used to gain a better understanding of the geochemical processes controlling the chemical composition of natural water. Several computer codes have been utilized to perform these calculations. Some of the more recent programs include MINEQL (Westall et al. 1976), PHREEQE (Parkhurst et al. 1980), WATEQ3 (Ball et al. 1981) and MINTEQ (Felmy et al. 1984). Several such computer programs have been successfully used to evaluate possible solid-phase controls on solution composition (Nordstrom et al. 1979), Gang and Langmuir 1974, Peterson and Krupka 1981, Peterson et al. 1982, and Deutsch et al. 1982). Geochemical modeling involving ion-speciation and solubility calculations (Peterson and Krupka 1981; Peterson et al. 1982) was used to verify if precipitation of solid phases in laboratory permeability columns was thermodynamically possible, and if so, what solids would be expected to precipitate. The results of the modeling efforts were then compared to mineralogical characterization studies performed on laboratory and field samples.

Little work, however, has been done in using geochemical computer codes to predict the aqueous phase compositions of solutions resulting from interaction with an assemblage of solid phases in a flow-through system. During such chemical interactions, one or more solid phases may dissolve and thermodynamically more stable solid phases precipitate as the solution composition changes. The new assemblage of solid phases can then be reacted with a new volume of influent solution and the process repeated.

A hypothesized assemblage of solid phases can be used to represent heterogeneous geologic materials, which are permitted to dissolve or precipitate in response to changes in the aqueous media. This conceptual model, in conjunction with the MINTEQ geochemical code, is then used to simulate the contact of a specified solution with these geologic materials. The resultant compositions of the aqueous phase and the change in mass of each solid phase in the assemblage

Table 1
Characterization of
the Morton Ranch Clay Sediment

Water content (g/g) (%) (after air drying)	4.10
Particle density (g/cm ³)	2.72
Particle Size	
Distribution (wt%)	
Sand (50-2000 μ m)	12.0
Silt (2-50 μ m)	54.0
Clay (<2 μ m)	34.0
pH of saturated paste	8.2
Eh of saturated paste (volts)	+0.406
EC of saturated extract (mmhos/cm)	0.70
Organic matter (g/g) (%)	1.44
CaCO ₃ (g/g) (%)	0.3*
Cation exchange capacity (CEC) (meq/100 g)	31.6

*Average of eight measurements

are calculated as successive pore volumes of solution interact with the solid phase assemblage.

Materials and Methods

The mineralogical alteration of sediments caused by contact with acidic tailings solution was evaluated from laboratory column experiments (Uziemblo et al. 1981, Peterson et al. 1982) and a study of field soil samples (Erikson and Sherwood 1982). The laboratory experiments involved the flow of Highland Mill tailings solution through Morton Ranch clay sediment for an 838-day period.

Table 1 lists the physical and chemical properties of the clay sediment obtained at the Morton Ranch mine in Wyoming. These materials were characterized using standard soil testing procedures as outlined in Black (1965a,b). Details of the experimental setup and methodology can be found in Gee et al. (1980a), Peterson et al. (1982), Serne et al. (1983) and Peterson et al. (1983).

The compositions of the tailings solutions used as influent for the column experiments are given in Table 2. The Highland Mill tailings solutions were taken from the Exxon Highland Mill in Wyoming. In general, the major cationic constituents were analyzed by inductively coupled plasma emission spectroscopy and the concentrations of trace elements were determined by graphite-furnace atomic absorption. Anionic components were analyzed by ion chromatography and titration; X-ray and γ -ray radio-analytical techniques were

Table 2
Composition (in mg/l) of Highland Mill
(H.M.) Tailings Solutions Used in Permeability
and Vacuum Extractor Columns

Constituent	H.M. Tailings solution #1 (used in permeability column)	H.M. Tailings solution #2 (used in vacuum extractor columns)
Li	0.9	0.48
B	0.19	0.19
HCO ₃ /CO ₃	0.0	0.0
NO ₃	16.5	8.5
F	4.0	4.0
Na	343	364
Mg	690	440
Al	600	396
Si	234	255
P	30	6.8
SO ₄	12,850	9,100
Cl	97	330
K	40	<3
Ca	537	483
V	10.6	10.6
Cr	2.7	1.5
Mn	64	43
Fe	2,215	560
Co	<1	1
Ni	3.0	1.7
Cu	2.3	1.3
Zn	8.4	3.9
As	3.50	0.45
Se	0.6	1.18
Sr	15.7	6.6
Mo	0.35	<0.05
Cd	0.04	0.04
Sb	<1	<1
Ba	<0.05	<0.05
La	ND*	5.0
Pb	<0.05	<0.04
U	40.0	7.2
pH	1.8	2.19
Eh (mV)	910	750

*ND - not determined.

used to measure radionuclide activities. A combination glass electrode was used to measure the pH of the tailings solutions and soil. The redox potential (e.g., Eh) of the solution was measured using a combination platinum-reference electrode. The pH and Eh values of the tailings solutions were determined on filtered (0.45 μ m membrane) samples.

The interaction of Morton Ranch clay sediments and Highland Mill tailings solution was studied in the laboratory using permeability and vacuum extractor columns. The permeability column was packed with the sediment from Morton Ranch to 96 percent of maximum compaction as determined by a standard

compaction test (Black 1965a). This resulted in a bulk density of 1.76 g/cm^3 for the sediment in this column. The permeability column was leached with the Highland Mill (H.M.) tailings solution (H.M. #1 in Table 2).

The vacuum extractor columns were packed with sediment from Morton Ranch to a density of 1.25 g/cm^3 . The material in the vacuum extractor columns was packed to a lower density than that in the permeability column to speed the movement of solution through the columns. The vacuum extractor experiments are described in Serne et al. (1983), and used solution H.M. #2 in Table 2 as a leachate. The contaminant concentrations found in the effluent solutions from these columns were compared to the modeling predictions.

At the conclusion of the experiments, the sediment column was dissected into five sections and the mineralogy of each section identified. In addition, sediment samples were collected to a depth of 60 cm below the bottom of an evaporation pond at the Lucky Mc Mill in Wyoming, which had been in contact with acidic mill tailings solution for approximately 10 years.

The mineralogy of all sediment samples was determined from bulk and/or clay-sized fractions using powder X-ray diffraction techniques. The clay-sized fraction of the sediments was separated from the bulk samples by sedimentation (Jackson 1956, 1979). X-ray diffractograms were obtained using $\text{CuK}\alpha$ radiation. The mineralogy of the field sediment samples from the Lucky Mc Mill was determined as a function of depth below the pond bottom. Mineralogical alteration of the sediments caused by reaction with the acidic leachates was evaluated by comparing diffractograms of contacted and uncontacted sediments.

Computer Modeling

The development of geochemical codes and their application to aqueous geochemical systems have been described in the reviews of Jenne (1981) and Mercer et al. (1981) and the compilation of geochemical modeling papers in Jenne (1979).

For the modeling calculations discussed in this paper, the MINTEQ geochemical code (Felmy et al. 1984) can be considered as having three parts: (1) a speciation submodel, (2) a solubility submodel, and (3) a mass transfer submodel. The calculations completed by each submodel, in turn, are dependent on the thermodynamic and reaction data stored in MINTEQ's thermodynamic data base. The sources of thermodynamic data in MINTEQ are described in Truesdell and Jones (1974), Ball et al. (1980, 1981), and in Krupka and Jenne (1982).

The speciation submodel first calculates the activities for the uncomplexed and complexed cationic, anionic and neutral species, and the distribution of these species among their redox states for a given water composition. Activities of individual aqueous species are corrected for ionic strength using the extended Debye-Hückel equation with two adjustable parameters (Truesdell and Jones 1974) or the Davies equation (Davies 1962, Ball et al. 1980).

After calculating the aqueous speciation, the solubility submodel then determines if the solution is at equilibrium with any of the minerals and other solids (including amorphous solids) in the MINTEQ thermodynamic data base. The solubility submodel calculates ion activity products (AP) from the activities of the aqueous species and the reaction stoichiometries for solids contained in the MINTEQ data base. These activity products (AP) are then compared to the equilibrium solubility products (K) stored in MINTEQ for these same solids, to test the assumption that certain of the dissolved constituents in the aqueous solution are in equilibrium with particular solid phases. Saturation indices ($\log [\text{AP}/\text{K}]$) are calculated to determine if the aqueous solution is at thermodynamic equilibrium ($\log [\text{AP}/\text{K}] = 0$), oversaturated ($\log [\text{AP}/\text{K}] > 0$), or undersaturated ($\log [\text{AP}/\text{K}] < 0$) with respect to a certain solid phase. If a solution is computed to be at equilibrium with a particular solid, then it is possible that the solid is precipitating or dissolving at a sufficient rate for it to control the concentration of certain of its constituents in that solution. If an aqueous solution is calculated to be oversaturated with respect to a certain solid phase, then it is inferred that kinetic and/or mineralogical factors prevent precipitation of the solid phase at a sufficient rate to significantly affect the concentration of dissolved constituents in the solution.

The results from the solubility submodel are then used by the mass transfer submodel of MINTEQ. If the solubility submodel indicates that a given solution is oversaturated with respect to a solid phase considered in the conceptual chemical model of the system, the mass transfer submodel will "precipitate" that solid phase until the solution is at equilibrium (i.e., $\log [\text{AP}/\text{K}] = 0$) with the solid. MINTEQ keeps track of the mass of precipitated material. If the solubility submodel computes a solution to be undersaturated with regard to a particular solid phase in the chemical model of the system, the MINTEQ mass-transfer submodel will "dissolve" that solid until solution equilibrium is achieved with respect to the solid, or until the finite mass of solid is completely dissolved.

The interaction of the acidic tailings solution with the clay sediment material was simulated by reacting incremental pore volumes of solution (H.M. Tailings Solution #2 in Table 2) with a hypothetical assemblage of solid phases, i.e., our conceptual model of the system. The solid phase assemblage consisted only of solids that could readily dissolve from the sediments or precipitate from solution. This was especially important because each pore volume of solution in the vacuum extractor columns was in contact with the sediments for only 16 hours. Because the MINTEQ computer code assumes a 1-liter volume of solution, the initial column pore volume of solution was multiplied by a scalar to convert a pore volume of solution to 1 liter of solution. The mass of solid in the column was then multiplied by this same scalar.

The solid phases included in the conceptual chemical model, their thermodynamic data and the sources

of these data are given in Table 3. Two of the most important criteria for selection of these solid phases were: (1) the rate of attainment of equilibrium of the solid with the solution, and (2) availability of accurate thermodynamic data for the solid. The rate of attainment of equilibrium was evaluated by reviewing the experimental literature. If these data were unavailable, the solid was considered if it has been identified as having formed under conditions similar to those present in these experiments. The only solid phase used in the chemical model to represent the sediment before contact with the acidic tailings solution was calcite (CaCO_3); the mass of calcite being determined from the carbonate analyses of the sediment (Table 1). The other solids shown in Table 3 were allowed to precipitate if they became oversaturated during the modeling simulation. The following constituents were included in the conceptual aqueous model: aluminum, calcium, carbonate, chloride, fluoride, iron, manganese, sodium, sulfate and magnesium.

Results and Discussion

Peterson et al. (1982) observed a decrease in permeability with time in laboratory permeability columns contacted with acidic uranium mill tailings solutions. These decreases in permeability were partially attributed to pore plugging resulting from the precipitation of minerals and amorphous solids. Other possible contributors to the decreases in permeability are examined in Peterson et al. (1982). In the first phase of this study (Peterson and Krupka 1981, Peterson et al. 1982), geochemical modeling (ion-speciation and

solubility computations) was used to verify if this precipitation was thermodynamically feasible, and if so, to predict which solids would be expected to precipitate. The predicted solids were then compared to minerals observed in a laboratory permeability column and in sediment from the evaporation pond at the Lucky Mc mine. The objective of the second phase of our study was to predict the changing solution concentrations of selected contaminants as uranium mill tailings solutions flowed through sediments.

Model-Predicted Solids vs. Observed Solids

X-ray Diffraction Analysis

The uncontacted sediments consist of a mixture of sand, silt and clay. The minerals identified in the uncontacted Morton Ranch clay sediments are feldspar ($[\text{K}, \text{Na}, \text{Ca}] [\text{Al}, \text{Si}]_4\text{O}_8$), illite ($\text{K}[\text{Al}, \text{Mg}, \text{Fe}]_2[\text{Si}, \text{Al}]_4\text{O}_{10}[\text{OH}]_2[\text{H}_2\text{O}]$), quartz (SiO_2), and smectite ($[\text{Na}, \text{Ca}]_{0.33}[\text{Al}, \text{Mg}]_2\text{Si}_4\text{O}_{10}[\text{OH}]_2 \cdot n\text{H}_2\text{O}$). These minerals were also identified in the field samples of uncontacted Lucky Mc alluvium. However, the Lucky Mc alluvium is strongly calcareous (U.S. NRC 1977), and, in addition, contains calcite (CaCO_3), dolomite ($[\text{Ca}, \text{Mg}] [\text{CO}_3]_2$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The total carbonate content of this native alluvium is estimated to be approximately 20 percent (Erikson and Sherwood 1982). No carbonate minerals were detected in X-ray diffractograms of Morton Ranch clay liner.

The permeability column was dissected after approximately 18 pore volumes of Highland Mill tailings solution (Solution 1 in Table 2) had flowed through

Table 3
Summary of Solids Considered in the Conceptual Chemical Model

Solid	Reaction	$\ln K_r^0, 298$	Reference
Jordanite	$\text{Al}^{3+} + 6\text{H}_2\text{O} + \text{SO}_4^{2-} \rightleftharpoons \text{Al}(\text{OH})_3 \cdot 5\text{H}_2\text{O} + \text{H}^+$	3.80	Nordstrom, D. K. 1982
Basaluminite (A) ^(a)	$4\text{Al}^{3+} + \text{SO}_4^{2-} + 15\text{H}_2\text{O} \rightleftharpoons 10\text{H}^+ + \text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$	-23.98	Nordstrom, D. K. 1982
$\text{Al}(\text{OH})_3(\text{A})$	$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3(\text{A}) + 3\text{H}^+$	-10.38	Truesdell, A. H. and B. F. Jones 1974
Gypsum	$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	4.60	(b)
Calcite	$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$	8.48	Plummer L. N. and E. Busenberg 1982
$\text{Fe}(\text{OH})_3(\text{A})$	$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3(\text{A}) + 3\text{H}^+$	-4.891	Truesdell, A. H. and B. F. Jones 1974
Siderite	$\text{Fe}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{FeCO}_3$	10.55	Truesdell, A. H. and B. F. Jones 1974
Pyrochroite	$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + \text{Mn}(\text{OH})_2$	-15.088	Ball et al. 1980
Rhodochrosite	$\text{Mn}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{MnCO}_3$	10.585	Johnson, K. S. 1982

(a) A = amorphous

(b) Letter from D. K. Nordstrom, U.S.G.S, Menlo Park, CA, to E. A. Jenne, Battelle Pacific Northwest Laboratories, Richland, WA, dated February 6, 1981.

the Morton Ranch clay liner over a period of 838 days. The extracted sediment was split into five sections perpendicular to the column axis; each section was 0.9cm thick.

The field sediment samples from the Lucky Mc mill were collected to a depth of 60cm while the evaporation pond was temporarily drained. The sediment profile was distinctly stratified with depth, based on color of the soil and measurement of the soil pH of the saturated pastes.

The results of the mineralogical studies (Uziemblo et al. 1981; Erikson and Sherwood 1982; and Peterson et al. 1982) suggest similar mineralogical alterations occurred in the laboratory column experiments and at the Lucky Mc field site. For example, the mineralogical changes with depth at the Lucky Mc site are schematically illustrated in Figure 1. The sample designations assigned to the field sediment samples are based on the location and depth from the pond bottom, the locations and abbreviations used are layered surface (LS), red sand (RS), 7400, northeast corner (NEC) and pipeline (P). The widths of the bars in Figure 1 indicate, qualitatively, the relative increase or decrease in proportions of the various minerals as estimated from the peak intensities on the diffractograms. The shallower field samples (LS, RS, 7400) are characterized by the complete dissolution of carbonates (calcite, dolomite) and the precipitation of two sulfates, jarosite and gypsum. Gypsum and jarosite were also identified as precipitates in the laboratory permeability column experiment. Although gypsum was present in the uncontacted Lucky Mc sediment, the number of X-ray peaks detected and the major peak intensities for gypsum significantly increased in the contacted samples. This suggests the formation of gypsum in the contacted soils in addition to that present in the uncontacted Lucky Mc sediment. Moreover, the X-ray diffraction data also indicate gypsum continues to form throughout the depth profile of the Lucky Mc evaporation pond (Figure 1) and throughout the permeability column.

Jarosite, however, is most concentrated in the shallower sediment from the Lucky Mc site (Figure 1, LS sample) where the sediment and tailings solution coexist at low pH (~3.0). The relative proportion of jarosite to the other detected minerals decreases with depth below the evaporation pond as the soil pH increases to 5.0 (7400 sample). Jarosite was not detected in deeper samples where the soil pH was > 5.0. A similar trend was noted in the column experiments (Peterson et al. 1982) in which jarosite was identified only in the two sections of soil nearest the influent end of the column.

The silicate minerals smectite, illite, kaolinite, quartz and feldspar are present in both the uncontacted Lucky Mc and Morton Ranch soils and were also identified in all of the contacted samples. This suggests the silicate minerals in the two sediments were not dissolved to a large extent, when reacted with acidic tailings solutions over the time frame of the laboratory experiment (838 days) and operation of the evapora-

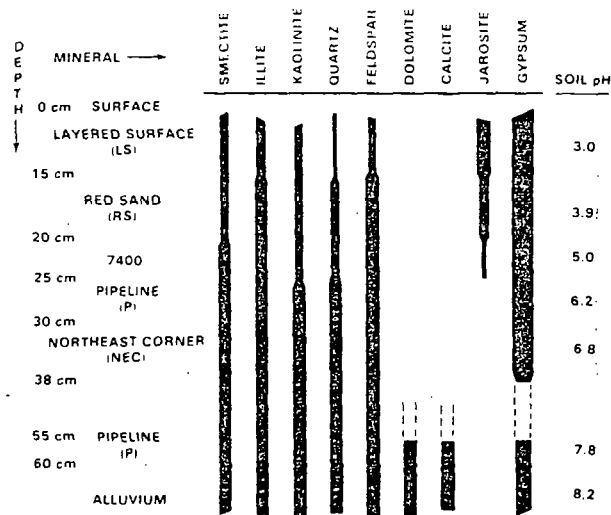


Figure 1. Mineralogical and soil pH profile as a function of depth beneath evaporation pond, Lucky Mc site, Gas Hills, Wyoming

tion pond at the Lucky Mc mill (10 years). The dissolution of carbonates and precipitation of secondary sulfate minerals (gypsum and jarosite), however, are the dominant processes occurring in the sediments contacting acidic tailings solutions. The general agreement between the mineralogical data from the laboratory and field results implies that field processes can be successfully simulated in the laboratory.

Geochemical Modeling

The solubility controls calculated using the MINTEQA code for effluent solutions from the permeability column are in good agreement with solid phases identified by X-ray diffraction analysis (Peterson et al. 1982). Ion speciation and solubility calculations indicated that the effluent solutions were in apparent equilibrium with the solid phases $\text{Fe}(\text{OH})_3(\text{A})$, $\text{Al}(\text{OH})_3(\text{A})$, celestite (SrSO_4), anglesite (PbSO_4), gypsum and alunite ($\text{KAl}_3[\text{SO}_4]_2[\text{OH}]_6$). Thus, the modeling results suggest that these solids could be precipitating and/or dissolving rapidly enough to control the concentrations of certain of their dissolved components.

The geochemical computer code computed all column effluent solutions, resulting from the interaction of H.M. tailings solution with the sediments to be oversaturated with respect to K-, Na- and H-jarosites ($\text{KFe}_3[\text{SO}_4]_2[\text{OH}]_6$, $\text{NaFe}_3[\text{SO}_4]_2[\text{OH}]_6$, $\text{HFe}_3[\text{SO}_4]_2[\text{OH}]_6$, respectively). These ion-speciation solubility calculations indicate the possibility of jarosite precipitation in these columns, though the attainment of equilibrium appears to be inhibited by kinetic and/or other constraints.

These results illustrate how geochemical modeling can be used, in parallel with mineralogical characteri-

zation techniques performed on laboratory and field samples, to identify the chemical reactions that are occurring in the uranium mill tailings/sediment system. The identification of jarosite and gypsum confirm the geochemical modeling predictions that these minerals formed when uranium mill tailings solutions contacted these sediments. In addition, modeling predicted the precipitation of several solids that could not be identified by X-ray diffraction because of the amorphous nature of some of these solids or the limited amount of material that precipitated.

A conclusion drawn from this portion of our work is that the geochemical modeling predictions and laboratory experiments were capable of simulating mineralogical changes that occurred in the field. Thus, the theoretical modeling predictions, laboratory experimental work and field studies are complementary.

Comparisons of Column Effluent Compositions with Model Predictions

A conceptual chemical model was formulated to represent the passage of reacting incremental pore volumes of tailings solution through the sediments. The predicted concentrations of contaminants were then compared to the experimental data at each pore volume. Results will be discussed for aluminum, manganese and calcium to demonstrate the utility of this approach for our system. In the results presented here, the pH and Eh were fixed at the observed values for each pore volume. Additional modeling results are discussed in Peterson et al. (1983).

Aluminum

Three aluminum solids (Table 3) were considered in the chemical model of the system: amorphous aluminum hydroxide [$\text{Al}(\text{OH})_3(\text{A})$], amorphous basaluminite [$\text{Al}_4(\text{SO}_4)\text{OH}_{10} \cdot 5\text{H}_2\text{O}(\text{A})$] and jurbanite [$\text{AlOHSO}_4 \cdot 5\text{H}_2\text{O}$]. The predicted aluminum concentrations (moles/l, molarity [M]) obtained by using these solids as solubility controls for aluminum are represented by the square symbols in Figure 2. The predicted aluminum concentrations closely follow the experimental concentrations (triangle symbols) in the first five pore volumes having high pH values but do not show the large increase in aluminum concentrations observed in the latter pore volumes for the experimental system. One explanation for the depressed values of the predicted aluminum concentrations in the latter pore volumes is due to the calculated precipitation of jurbanite. Jurbanite is the most thermodynamically stable solid phase (of the three considered) at these latter pore volumes, but could not be precipitating at a sufficient rate to significantly affect the concentration of dissolved aluminum.

Therefore, jurbanite was excluded from our second chemical model of the aluminum system because of possible kinetic constraints. The second aluminum model contained only amorphous aluminum hydroxide and amorphous basaluminite as potential solubility

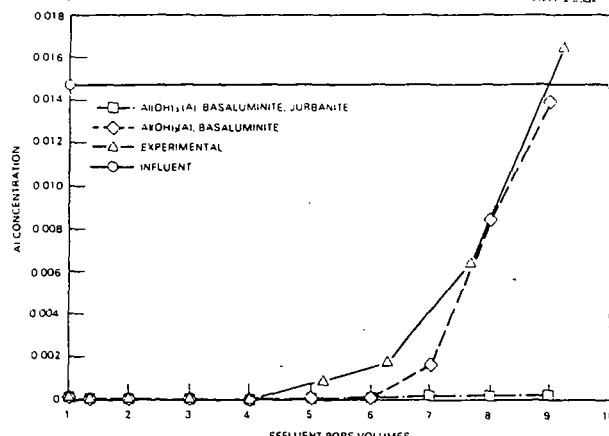


Figure 2. Predicted and experimental aqueous aluminum concentrations (M) with measured pH and Eh values

controls for the dissolved aluminum concentrations. In these modeling results, amorphous aluminum hydroxide precipitates in the first pore volume and basaluminite precipitates in pore volumes 2 through 9. The predicted aluminum concentrations are extremely close to the experimental results. Thus, a chemical model consisting of amorphous aluminum hydroxide and amorphous basaluminite provides an accurate model of the experimentally observed aluminum concentrations for the tailings solution/sediment system. Formation of amorphous basaluminite is supported by Nordström (1982), who concluded that amorphous basaluminite is likely to precipitate from acid sulfate solutions and may persist for long periods of time.

Manganese

Predicted vs. experimental manganese concentrations are shown in Figure 3. Rhodochrosite was the only manganese solid predicted to precipitate of those manganese solids considered in the chemical model (Table 3). In the chemical model, rhodochrosite precipitated in the first three pore volumes, began to dissolve at pore volume four, and completely redissolved at pore volume five. After the fifth pore volume, predicted manganese concentrations fell to the influent values. The experimental values show the same general trends as the predicted values, i.e., lower concentrations than the influent values at early pore volumes, higher than influent values at intermediate pore volumes and concentrations that decrease toward the influent values at latter pore volumes.

Therefore, a chemical model that included the precipitation and dissolution of rhodochrosite, was able to predict the manganese concentration trends that were observed in the experimental data. The predicted manganese concentrations, however, did not exactly match the observed effluent curve.

Calcium

The chemical model included calcite and gypsum

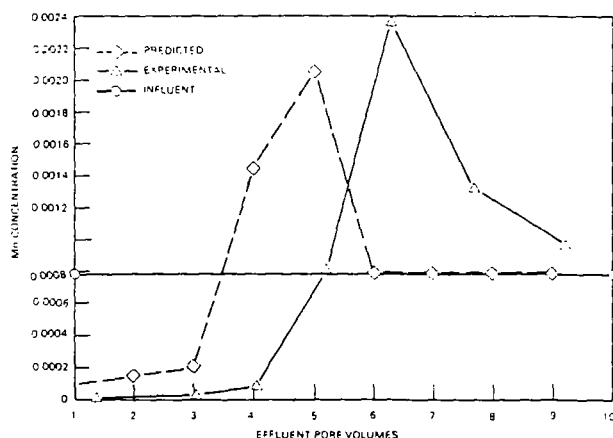


Figure 3. Predicted and experimental manganese concentrations (M) with measured pH and Eh

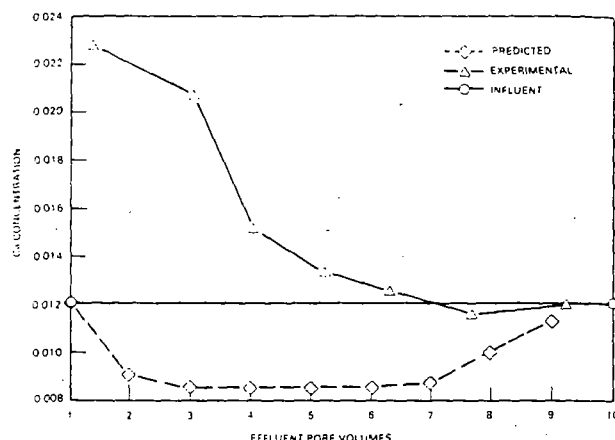


Figure 4. Predicted and experimental aqueous calcium concentrations (M) with measured pH and Eh values

as possible solubility controls for calcium.

The predicted and experimental concentrations of calcium are shown in Figure 4. The predicted calcium concentrations are always less than the experimental concentrations; this is exactly opposite of the pattern predicted for sulfate concentrations. In the first pore volume, the predicted calcium concentration is 0.01 molar lower than the experimental value, and the predicted sulfate concentration approximately 0.01 molar higher than the experimental value. Thus, in both cases, the activity product of gypsum is being satisfied. Ion exchange or desorption of calcium from the sediments would not increase the predicted aqueous calcium concentration because the calcium released from the sediments would precipitate as calcite and gypsum in the chemical model.

Another possible explanation for the differences between the modeling and experimental systems is that the calcium carbonate phase actually present in the sediments was more soluble than end-member calcite. The high magnesium concentrations in the column effluents suggest the possible presence of a magnesium-substituted calcite. Magnesian calcites have a greater solubility than pure calcium carbonates (Thorstenson and Plummer 1977). The substitution of a magnesian calcite, for a pure end-member calcite, into the chemical model allowed us to predict the initial high concentrations of calcium that were observed in the experimental system. The dissolution of dolomite has been considered in other modeling studies of these systems (Peterson et al. 1983). The calcium-sulfate system demonstrates the ability of geochemical modeling to test the adequacy of proposed mechanisms and to suggest additional plausible mechanisms.

Conclusions

Decreases in permeability noted in permeability columns were partially attributed to the precipitation of solid phases, which plugged the pores of sediments. Geochemical modeling predicts, and X-ray character-

ization confirms, that precipitation of solids from solution is occurring in the acidic tailings solution and sediment interactions studied. X-ray diffraction identified gypsum and an alunite-group mineral, such as jarosite, as having precipitated after acidic tailings solutions reacted with clay liners and sediments. Geochemical modeling predicted that these same phases should be precipitating, along with several amorphous solids not identifiable by X-ray diffraction. The same mineralogical changes observed in the laboratory sediment columns were found at a drained evaporation pond with a 10-year history of acid attack. The observed minerals were also predicted, from geochemical (thermodynamic) modeling, to form upon neutralization of the acidic tailings solutions by the contacted sediments. This approach illustrates how geochemical modeling can be used, in parallel with mineralogical characterization techniques performed on laboratory and field studies, to delineate the chemical reactions that may change the permeability of liner materials.

Aqueous/sediment interactions are extremely complex. Predictive geochemical modeling was effective in unraveling some of the predominant mechanisms controlling the concentrations of certain dissolved constituents. The geochemical modeling can be used to quantitatively evaluate: (1) the accuracy of theorized chemical models of complex aqueous/sediment interactions, and (2) the predominant reactions affecting the composition of the aqueous phase.

The precipitation/dissolution reactions considered in the conceptual model were capable of predicting the column effluent concentrations of several major constituents in the tailings solutions (e.g., SO_4 , Ca, Al, Mn, and Fe; Peterson et al. 1983). Sulfate concentrations in the column effluents were generally one to two orders of magnitude above the secondary drinking water standards established by the U.S. Environmental Protection Agency. The conceptual model was able to predict these elevated concentrations. No solubility controls, however, were identified for the majority of the trace constituents. Many trace constituents appear to be controlled by adsorption on and/or co-precipita-

tion with ferric oxyhydroxide solids (Serne et al. 1983). More work, namely incorporation of trace metal adsorption reactions, is necessary to predict the migration of other contaminants from uranium mill tailings solution. The geochemical modeling approach coupled with laboratory and field studies should be applicable to a variety of waste disposal problems.

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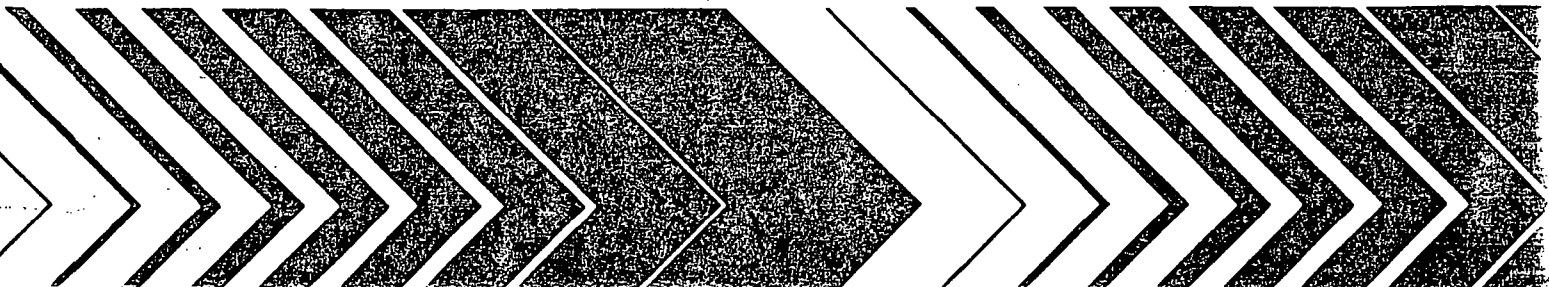
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PHYSICAL AND CHEMICAL ATTENUATION PROPERTIES OF TIDAL MARSH SOILS
AT THREE MUNICIPAL LANDFILL SITES

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ABSTRACT

The hydraulic conductivity, (K), cation exchange capacity, (CEC), and total organic carbon, (TOC), of soils composed of clays and silts are thought to make them effective barriers to contaminants in groundwater, and media capable of sorbing heavy metals and organic compounds. Tidal marsh deposits consisting of silts and clays and underlying sands at three municipal landfills were tested for pH, CEC, TOC and K. Results were compared with heavy metal and organic compound concentrations measured in groundwater samples above and below the tidal marsh deposits. Evaluation indicated that the tidal marsh desposits were less effective in removing heavy metals than expected, but were effective in preventing migration of organic compounds into underlying sand deposits. Total volatile organics, (TVO), and total halogenated volatile organics, (TVHO), were reduced from 72,440 ug/l to 27 ug/l, and 867 ug/l to <10 ug/l in some cases. Organic carbon content in the tidal marsh deposits averaged 2.2%. Decomposition of the organic fraction yielded acids which reduced pH to as low as 3.3. Consequently, the tidal marsh deposits were ineffective in removing heavy metals, but remained effective as an hydraulic barrier. Our studies showed that the soils effectiveness to mitigate groundwater degradation from heavy metals and organics can be gauged by evaluating the soil's chemical and physical properties.

INTRODUCTION AND PURPOSE

Tidal marsh deposits consisting of organic silt and clay are generally considered effective hydraulic barriers to ground water flow and having the adsorptive capacity to retain dissolved heavy metals and organics. However, natural factors may alter, negate or reduce these properties.

Such factors include:

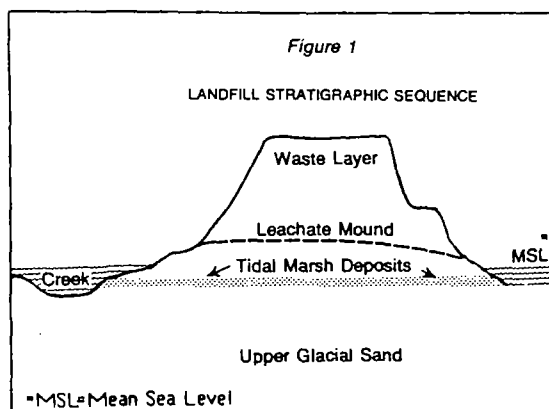
- Soil pH, cation exchange capacity, and total organic carbon
- Inclusions in the deposits (pockets of sand and/or shell fragments)
- Discontinuities within the silt and clay deposit

- Hydraulic conductivity of deposits

This paper addresses our findings on soil pH, CEC, and TOC and their effects on the adsorptive capacity of tidal marsh deposits.

Gibbs & Hill completed a hydrogeologic study at three municipal landfills located in the New York Metropolitan area. The investigation aimed at assessing the impacts of landfill-generated leachate on local aquifers and bay waters.

At each landfill, the stratigraphic sequence consisted of the following (see Figure 1):



- Municipal waste: 30' to 120'
- Tidal marsh deposits: 5'-12'
- Hydraulic fill: 5'
- Wisconsin-Age glacial outwash sediments (Upper Glacial sand aquifer) to 150'
- Other Pleistocene and Cretaceous Sediments
- Pre-Cambrian crystalline bedrock

The aquifers underlying each site are:

- Water Table Aquifer: (Leachate Mound)
- Confined Aquifers: Upper Glacial, Jameco, Magothy, and Lloyd (top to bottom)

Of these aquifers, the study focused on the Upper Glacial.

Ground water level measurements within the aquifers varied as follows:

- Leachate mound: 8' to 11' MSL (Mean Sea Level)
- Upper Glacial Aquifer: -2 to -6' MSL

The difference between piezometric heads caused a downward driving force, which resulted in leakage of ground water and landfill leachate from the leachate mound into the Upper Glacial Aquifer, through the tidal marsh deposit.

Chemical soil testing was performed on samples from the tidal marsh deposits and the Upper Glacial sands. The tidal marsh deposits consisted primarily of silt and clay with occasional lenses of fine sand and shells. Organic content included humic materials and layers of peat. The Upper Glacial sands were composed mainly of sand and gravel.

Municipal refuse makes up the bulk of the material disposed at the landfills. Daily disposal rates run as high as 9,500 tons at the largest landfill, 297 acres. Waste oil was applied to landfill roads in earlier years to control road dust. Illegal dumping of hazardous wastes occurred at all three sites; and 5,000 fifty-five gallon drums containing wastes of paint pigments and solvents, were recently unearthed at one location and

waste oil laced with PCB's at another.

APPROACH

Fifteen soil samples were obtained during the installation of ground water monitoring wells. Samples were collected using a steel split-spoon sampler and undisturbed samples were retrieved using a brass thin wall "shelby" tube.

Samples were sent to the lab and analyzed for:

- pH
- Cation Exchange Capacity (CEC)
- Total Organic Carbon (TOC)
- Hydraulic conductivity (K)
- Grain size distribution and identification.

Well water samples from above (U wells), and below (S wells), the tidal marsh deposits were compared for heavy metals and organics. The results were then examined against soil sample test results, and the physical character of the tidal marsh deposits. We gauged the effectiveness of the tidal marsh deposits to filter heavy metals and organics based on these comparisons.

A total of 65 wells were used in this study. Wells above the tidal marsh deposits numbered 32 and were located between +1.0 and -7.0 mean sea level - just above the deposits. The 23 S wells were placed between -30 and -40 feet below mean sea level in the Upper Glacial Aquifer. The remaining 10 wells were placed in the Upper Glacial

Aquifer between -110 and -140 feet below mean sea level.

EVALUATION FACTORS/PROBLEMS

A number of factors are extremely important to consider when assessing the potential of the deposits to mitigate wastes. First, the information obtained may be used to obtain a relative measure of effectiveness against chemical migration. Second, in order to properly evaluate the soil chemical data, it is essential to get an accurate picture of the deposits.

Large voids, windows or significant layers of coarse materials allow ready movement of leachate from one layer to another. If these are not recognized and their dimensions and character known, even favorable CEC, pH and TOC data may yield erroneous interpretations. In addition, undisturbed samples should be examined to see what portions are the most frequently occurring, and which portions show the outside range of variability in the samples. Third, it is important to test CEC at ambient pH in addition to pH 7. This is important because the soils should be evaluated under in-situ conditions, conditions unlikely to change in the near future.

One problem we had was the lack of leachate extraction analyses on the soil samples. This information would have given a better account of where the metals and organics were moving and how much was being sorbed.

RESULTS

Cation Exchange Capacity

The tidal marsh deposits samples had CEC values of 7.0 to 237 milliequivalents (me)/100g soil, with most values falling

between 39 and 184 me/100g. These values are relatively high and were attributed to humus content of the soil.

CEC values in the Upper Glacial sand ranged from 0.6 to 59 me/100g, with an average CEC of 22 me/100g.

Overall, CEC values in the tidal marsh deposits were one order of magnitude greater than in the Upper Glacial sands (See Table 1).

TABLE 1A
TIDAL MARSH DEPOSITS
SOILS CHEMISTRY: pH, TOC, CEC

Sample Data	Landfill 1			Landfill 2		Landfill 3	
Well No.	HF102D	HF111	HF201	HP203U	HE202S	HE203S	HE203S
pH	3.6	3.8	3.5	5.5	3.5	4.8	3.3
TOC, ug/g	27,100	14,900	1,600	20,800	7,580	1,010	25,500
CEC, meq/100g @ pH 7	184	237	24	175	39	7	180
Material Type	ML-1	ML-2	SM-SC	ML-CL	CL	ML-3	ML-4

Material Type:

ML-1: Soft grey silt, some clay, trace shell fragments.
ML-2: Soft grey silt, little clay, trace peat.
SM-SC: Olive brown medium sand, some silt grading to well graded sand with trace silt, clay and gravel.
ML-CL: Silt and Clay with an eight inch layer of shell fragments.
CL: Clay with some silt, trace fine sand, grading to fine sand and little silt.
ML-3: Silt with little clay and shell fragments, trace very fine sand.
ML-4: Silt and clay.

TABLE 1B
UPPER GLACIAL SANDS AQUIFER
SOILS CHEMISTRY: pH, TOC, CEC

Sample Data	Landfill 1			Landfill 2			Landfill 3	
Well No.	HF102D*	HF115	HF201S	HP201	HP203	HP204	HE202S	HE204S
pH	3.5	6.6	6.0	5.9	6.1	6.5	3.0	8.3
TOC, ug/g	550	410	750	600	420	960	320	780
CEC, meq/100g @ pH 7	20	59	152**	0.6	8	13	47	4
Material Type	SM-1	SM-2	SP-SW	SW-SP	SW	SM-3	SM-4	SM-SW

* Above Tidal Marsh Deposits - Not part of Upper Glacial Sands Aquifer

** Possible sample contamination

Material Type:

SM-1: Brown fine to medium sand, dense, little silt.
SM-2: Brown medium to coarse sand, moderately dense, little silt.
SP-SW: Grey medium to coarse sand, slightly dense with trace silt and some gravel.
SW-SP: Grey medium to coarse sand, slightly dense, trace silt and fine gravel.
SW: Fine to coarse sand with trace silt and fine gravel.
SM-3: Olive brown medium to coarse sand, loose, with trace silt and brick fragments.
SM-4: Fine to medium sand with some silt.
SM-SW: Fine to coarse sand with trace silt.

Soil pH

Low values for soil pH (acid conditions) indicated increased potential for mobility of metallic ions.

Tidal marsh deposits samples exhibited soil pH values of 3.3 to 5.5, with most of the samples being extremely acid (pH <4.5) (USDA, 1951). pH in the Upper Glacial sands ranged from extremely acid to moderately alkaline (pH 3.0-8.3), but most samples were in the medium to slightly acid range (pH 5.6 to 6.6).

Lower pH values in the tidal marsh deposits were attributed to acids produced from decomposing organic matter.

The pH in groundwater samples above the tidal marsh deposits ranged between 6.3 and 7.8. Below these deposits they ranged between 6.2 and 7.4.

Soil Organic Carbon

The organic carbon content affects a soil's potential to remove contaminants by providing sites for ion exchange and adsorption, as well as enhancing its capacity to filter out suspended particles, such as PCB's (Weber et al, 1983).

TOC content of the tidal marsh deposits ranged between 0.10 to 2.7%, with an average of approximately 2.2%.

The TOC of the Upper Glacial sands was much lower, ranging between 0.03 and 0.16%, with an average of 0.07%.

Relationship between pH, TOC and CEC

A balance exists in the soil between the pH, CEC and organic matter content. The two components of CEC are:

- pH-independent CEC:

This component is determined by the cations which are fixed in the soil mineral during formation.

- pH-dependent CEC:

This component is related primarily to the organic fraction of the soil, particularly organic functional groups associated with the humus. As the pH increases above 5, these groups increase their ability to adsorb metallic ions.

The tidal marsh deposits in our study included both CEC components. Four samples with TOC content greater than 1% had high CEC values of 175 to 237 me/100g. Three samples with less than 1% TOC content had CEC's of 7.0 to 39 me/100g.

The Upper Glacial sands had little or no organic matter content, and low CEC values. TOC ranged from 0.03 to 0.1% and CEC values ranged from 0.6 to 59 me/100g. Consequently, CEC values in the Upper Glacial sand layers were mostly pH-independent.

Soil Attenuation Potential

Soil attenuation potential results from a combination of chemical and physical factors. Due to the large differences in pH, CEC, TOC and physical characteristics, attenuation in the tidal marsh deposits and Upper Glacial sands in our study differed as discussed below.

Tidal Marsh Deposits

Attenuation potential

appeared to be limited. Despite thickness (5' to 12') and relatively high TOC (>1%), the water quality data did not show any consistent reduction of heavy metals attributable to this layer, as evidenced by a comparison of heavy metal concentrations between water samples from above and below the tidal marsh deposits.

At landfill 1, Ni concentrations at 102U were 50 ug/l and 276 ug/l at 102S. In well 104U, Cr concentration was 38 ug/l, while at 104S it was 32 ug/l. At landfill 2, Sb concentrations in 101U were 540 ug/l and 500 ug/l at 101S. At 103U Cd was 28 ug/l and 38 ug/l at 103S (See Table 2).

Heavy metal concentrations in groundwater samples were generally one order of magnitude greater than background bay water samples taken near the bay center and inlet. Background bay water samples taken near the landfill were generally close in heavy metal content to the groundwater samples. Tidal fluctuations, which bring bay water through the Upper Glacial sands toward the landfills, may explain why some wells show concentrations of heavy metals which are greater below the tidal marsh deposits than above. It is also possible that very low pH levels are causing a release of metals at some locations.

Measurements taken at monitoring wells above the tidal marsh deposits showed the effect of tidal fluctuations on the leachate mound to be negligible. Below the tidal marsh deposits groundwater levels ranged between 0.95 and 2.57 feet.

TABLE 2
1984 GROUNDWATER QUALITY, (ug/l and pH in units)

LANDFILL 1													
Well, HF:	Sb (100)	As (2)	Be (10)	Cd (4)	Cr (20)	Cu (20)	Pb (40)	Hg (0.2)	Ni (40)	Se (2)	Ag (40)	Th (100)	pH
101 U	L	L	L	8	L	L	80	L	94	L	L	L	84 7.8
101 S	100	L	L	10	L	L	L	L	92	L	L	L	48 6.6
102 U	L	L	L	L	L	L	L	L	50	L	L	L	30 6.8
102 S	460	L	L	40	32	L	240	L	276	L	L	L	52 6.7
103 U	L	6	L	6	L	54	L	L	L	L	L	L	68 6.9
103 S	240	L	L	26	26	76	140	L	210	L	L	220	58 6.8
104 U	L	L	L	20	38	74	80	L	160	L	L	120	358 7.5
104 S	220	L	L	36	32	70	200	L	274	L	L	340	52 7.0
201 U	L	6	L	6	46	50	60	L	198	L	L	L	78 7.7
201 S	220	L	L	21	28	57	170	L	198	L	L	240	43 6.6

LANDFILL 2													
Well, HF:	Sb (100)	As (2)	Be (10)	Cd (4)	Cr (20)	Cu (20)	Pb (40)	Hg (0.2)	Ni (40)	Se (2)	Ag (40)	Th (100)	pH
101 U	540	L	L	40	62	50	140	2	112	L	L	L	72 6.7
101 S	500	L	L	18	48	L	40	L	94	L	L	L	46 7.2
102 U	200	6	L	26	38	L	120	L	46	L	L	L	28 7.2
102 S	L	L	L	L	L	L	L	L	L	L	L	L	6 6.5
103 U	L	L	L	28	26	L	100	L	56	L	L	L	62 7.0
103 S	400	L	L	38	52	L	220	L	110	L	L	L	66 6.7
201 U	L	L	L	6	22	L	60	L	224	L	L	140	104 7.4
201 S	180	L	L	14	20	L	120	L	188	L	L	L	56 6.2
203 U	L	L	L	26	28	L	120	L	60	L	L	L	96 7.0
203 S	380	L	L	36	46	L	180	4	90	L	L	L	56 7.0

LANDFILL 3													
Well, HF:	Sb (100)	As (2)	Be (10)	Cd (4)	Cr (20)	Cu (20)	Pb (40)	Hg (0.2)	Ni (40)	Se (2)	Ag (40)	Th (100)	pH
3N(S)	-	-	-	20	-	-	100	L	-	-	-	-	66 7.5
3S(U)	-	-	-	6	-	-	L	L	-	-	-	-	54 5.7
101 U	L	L	L	L	L	L	80	L	L	L	L	L	70 6.3
101 S	140	L	L	18	24	L	L	0.48	L	L	L	L	96 6.7
102 U	320	L	L	L	22	L	80	L	L	L	L	L	82 7.0
102 S	760	L	L	10	24	L	80	L	52	L	L	L	72 7.1
103 U	120	L	L	L	24	L	60	L	50	L	L	L	140 6.9
103 S	1,560	L	L	46	58	L	260	L	240	L	L	340	114 7.3
202 U	220	L	L	L	L	L	L	L	L	L	L	L	132 6.7
202 S	L	L	L	L	L	L	L	L	L	L	L	L	54 7.0
203 U	-	L	L	30	-	L	100	L	-	-	-	-	10 7.2
203 S	-	-	-	30	-	-	L	L	-	-	-	-	304 7.4

L = Less than detection limit
() = Detection limit

The lack of contaminant removal by the tidal marsh deposits is believed to be due to:

- High acidity in the tidal marsh deposits which lowers the effective CEC.
- High concentrations of Na, Al and Mn present in the bay water, and released from soil at low pH, compete for adsorption sites.

- Reduction and subsequent increased mobility of cations caused by saturated (anerobic) conditions.
- Physical gaps and inclusions of more permeable sediments in the tidal marsh deposits allow leachate to percolate directly into the Upper Glacial sands.

Large differences in concentrations of total volatile organics were found in water above and below tidal marsh deposits. It appeared that the relatively high TOC content of the tidal marsh deposits caused this reduction; a result of the affinity of organic material in the deposits for hydrophobic compounds contained in leachate (See Table 3).

TABLE 3

TOTAL VOLATILE ORGANICS (TVO)
TOTAL VOLATILE HALOGENATED ORGANICS (TVHO)

Land-fill	Well	TVO (10)	TVHO (10)
3	3 N S	246	L
3	3 N U	L	L
3	101 U	49,083	31,775
3	101 S	3,390	2,549
3	103 U	L	L
3	103 S	181	L
2	102 U	1,540	82
2	102 S	L	L
2	201 U	72,440	867
2	201 S	27	L

L = Less than Detection Limit
() = Detection Limit
U = Well in Leachate Mound
S = Well in Upper Glacial Sand
Values in ug/l

Upper Glacial Sand

The Upper Glacial sand layer has a very low potential for attenuating the passage of contaminants because of:

- Large particles size (low clay content) and low CEC
- Low organic matter content

These factors result in a medium which has little or no capacity to attenuate wastes.

SUMMARY

Overall attenuation potential in the tidal marsh deposits was low. Unfavorable pH, high concentrations of competing ions, and anerobic conditions resulted in deposits which have a low capacity to attenuate heavy metals in leachate. The tidal marsh deposits apparently accomplished some removal of dissolved organic compounds, but the most significant effect was the physical restriction of the vertical flow of leachate from the landfill to Upper Glacial sand.

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